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ON THE OXIDATION OF BENZENE DERIVATIVES WITH POTASSIUM FERRICYANIDE.[1]

BY W. A. NOYES.

II.

Whether ortho-brom-toluene can be oxidised by potassium ferricyanide in alkaline solution or not, was left undecided by the experiments described in my first paper. I have now repeated the experiments, using for the purpose pure ortho-brom-toluene, and find that it can be oxidised to ortho-brom-benzoic acid by the agent in question. The oxidation, however, takes place with great difficulty.

The ortho-brom-toluene was prepared from ortho-toluidine by the method described by Jackson.[2] The ortho-toluidine used was obtained from Schuchardt in Goerlitz, and gave, on heating in a sealed tube with glacial acetic acid, an acettoluid which fused at 107°. The crude ortho-brom-toluene at first obtained was heated on the water-bath for five hours with a mixture of potassium bichromate, sulphuric acid and water. After separating from the oxidising mixture it was distilled from a solution of caustic potash with water vapor.

The oxidation was conducted as described in my first paper. One gram of the ortho-brom-toluene with a mixture of 25 grams of potassium ferricyanide, 12 grams of caustic potash and 100

[1] This Journal **5**, 97. [2] *Ibid.* **1**, 100.

grams of water were boiled for three or four hours with an inverted condenser. The unoxidised brom-toluene was then distilled with water vapor. The solution left was filtered from ferric oxide, which always separated, the filtrate was evaporated somewhat, and part of the potassium ferrocyanide was crystallised out. The crystals of ferrocyanide were filtered off and washed once or twice with cold water. The filtrate and washings were acidified with hydrochloric acid and extracted with ether. The ether was distilled off, the residue was dissolved in a little ether, and the solution evaporated on a weighed watch-glass. The residues obtained in this way in three different experiments weighed, respectively, 4.3, 5 and 3.9 milligrams. The residues obtained by the oxidation of para-brom-toluene under the same conditions weighed in two experiments 6.4 and 6.5 milligrams.

Of course these residues cannot be considered as pure in either case, but the results obtained indicate that ortho-brom-toluene is oxidised more slowly than para-brom-toluene, by potassium ferricyanide.

In order to obtain enough of the ortho-brom-benzoic acid to establish its existence in the residues mentioned above, six grams of ortho-brom-toluene were oxidised in lots of one gram each. The acid obtained was converted into the barium salt and the solution of the salt was evaporated to dryness. The residue was treated with alcohol and filtered, the filtrate was evaporated to dryness, the residue dissolved in a little water, and the ortho-brom-benzoic acid precipitated with hydrochloric acid and recrystallised from water. It fused at 144°–145°, hence lacked a little of being perfectly pure. However, under the circumstances there could be no reasonable doubt as to its identity, and it was not thought profitable to spend further time on this point. The presence of bromine in the acid was established by qualitative tests.

Oxidation of para-toluene-sulphamide.

In studying the oxidising action of chromic acid on benzene derivatives, Remsen and his colleagues have found the sulphamide derivatives especially suitable for the purpose, on account of the properties of the acids obtained by their oxidation. It was thought desirable, accordingly, to include some of these substances in the study of the oxidising action of potassium ferricyanide.

The para-sulphamide of toluene was prepared from toluene in

the usual way by conversion into the sulphonic acid and successive treatment of the potassium salt of the latter with phosphorus pentachloride and ammonia. After crystallising from water the amide fused at 136°.

Two grams of the amide were boiled for three hours with 20 grams of caustic potash, 50 grams of potassium ferricyanide and 200 cc. of water. The filtrate from the ferric oxide was concentrated and part of the potassium ferrocyanide crystallised out. On acidifying the filtrate from the ferrocyanide with hydrochloric acid, a precipitate of para-sulphamine-benzoic acid, mixed with unoxidised toluene-sulphamide, was obtained. The solution of the barium salt obtained by boiling with barium carbonate was evaporated to dryness, and the residue was treated four times with strong alcohol to remove the sulphamide still mixed with the salt. The purified salt was then dissolved in hot water, filtered, and the filtrate cooled quickly. The salt separated in peculiar ball-like masses. These were separated from the mother liquors, washed slightly, and allowed to stand loosely covered for two days till air-dry. The salt was analysed with the following results:

0.2103 gram of the salt lost 0.0309 gram H_2O at 160°, and gave 0.0770 gram $BaSO_4$.

	Calculated.		Found.
$(C_7H_6SO_4N)_2$	400	63.80	...
Ba	137	21.85	21.53
$5H_2O$	90	14.35	14.69

The purified barium salt obtained by a second oxidation conducted in the same manner as the first, was dissolved in water and the acid precipitated with hydrochloric acid. The acid was recrystallised from water and analysed.

0.1567 gram of the acid gave 0.01141 gram N (Frankland's method).

	Calculated for $C_7H_7SO_4N$.	Found.
N	6.97	7.28

The acid was nearly insoluble in cold water, and soluble with difficulty in hot water. It began to fuse with decomposition at about 280°.

A rough estimate of the yield was made with the second oxidation. From two grams of para-toluene-sulphamide there was obtained by precipitation from the purified barium salt about 1.1 grams of the acid.

The analyses given above could leave no doubt that para-sulphamine-benzoic acid is formed by the oxidation of para-toluene-sulphamide with potassium ferricyanide. However, as Remsen[1] reports in his analysis of the barium salt of this acid *one* molecule of water instead of *five*, as found by myself, I thought best to oxidise some of the para-amide in the manner described by him,[2] with potassium bichromate and sulphuric acid, and make a more careful study of the barium salt of the acid obtained in that way.

The oxidation was conducted exactly as described by Remsen. After converting into the barium salt, the solution of the latter was evaporated to dryness, and the residue was treated several times with strong alcohol to remove any unoxidised amide which it might contain.

On crystallising from water some difficulty was found in obtaining salts of definite composition. It was finally established that if a hot solution of the salt was allowed to stand still so that no crystals were formed, until it was cold, a salt separated in ball-like masses containing five molecules of water; on the other hand, if the salt crystallised out while the solution was still warm, the crystals were in the form of small scales with a pearly lustre and contained two molecules of water. It was found that the salt with five molecules of water lost a large part of its water quite rapidly on standing over sulphuric acid. The last portions of the water were given off more slowly, but the salt became almost anhydrous by long standing (one month) over sulphuric acid. In all probability this is the salt which Remsen prepared, and on drying it over sulphuric acid he happened to leave it just long enough so that all but one molecule of water was given off.

The analyses of the salts were as follows:

0.1265 gram of the salt which separated from the cold solution lost 0.0185 gram H_2O at 180°, and gave 0.0474 gram $BaSO_4$.

	Calculated.	Found.
Ba	21.85	21.88
$5H_2O$	14.35	14.51

I. 0.1697 gram of the salt which crystallised in scales from a warm solution lost 0.0108 gram H_2O at 170°, and gave 0.0692 gram $BaSO_4$.

[1] Annalen der Chemie **178**, 302. [2] *Ibid.* **178**, 297.

II. 0.1302 gram of the salt lost 0.0084 gram H_2O at 170°, and gave 0.0524 gram $BaSO_4$.

	Calculated.	Found. I.	Found. II.
Ba	23.91	23.98	23.65
H_2O	6.28	6.36	6.45

OXIDATION OF META-NITRO-TOLUENE.

By W. A. Noyes and W. E. Moses.

In the experiments described by one of us it was shown that both ortho- and para-nitro-toluene are quite easily oxidised by potassium ferricyanide and caustic potash, while toluene itself is oxidised with great difficulty. In other words, the nitro group when in the ortho or para position with reference to the methyl of toluene, causes that methyl to be very much more easily attacked by this oxidising agent. The question whether a nitro group in the meta position with reference to the methyl would have the same effect was naturally suggested. The experiments here described were undertaken to determine that point.

The meta-nitro-toluene was prepared from para-toluidine. This was converted into para-acettoluid by heating in sealed tubes for two hours with twice the weight of glacial acetic acid. The temperature used was 150°–160°, and the yield was almost quantitative. The nitro group was introduced as described by Cosack.[1] Ten grams of the para-acettoluid were put in a flask with 45 grams of glacial acetic acid, and a little more than the calculated amount of nitric acid, sp. gr. 1.50 or above, was added. It was found that if the acetic acid contained a little water, or if the nitric acid was a little weaker, the nitration was unsuccessful. The meta-nitro-para-acettoluid was recrystallised from water. The acetyl group was split off by boiling with caustic potash, and the amido compound was recrystallised from alcohol.

The amido group was eliminated as described by Goldschmidt.[2] The meta-nitro-toluidine was suspended in absolute alcohol, and nitrous anhydride was passed in until the odor of nitrous ether was strongly marked. The diazo compound formed was decomposed by heating on the water-bath, and the excess of alcohol and nitrous

[1] Berichte der deutschen chemischen Gesellschaft **13**, 1088. [2] *Ibid.* **11**, 1625.

ether were distilled off. The meta-nitro-toluene was then distilled over in a current of steam. It was redistilled once or twice in the same way to purify it. Thus prepared it solidified on cooling nearly to 0°, and melted again at 16°.

For the purpose of a more exact comparison the oxidation of ortho- and para-nitro-toluene was repeated. The para-nitro-toluene used was obtained from Kahlbaum and fused at 54°. The ortho-nitro-toluene was prepared from para-toluidine by nitrating as recently described by Nölting and Collin.[1] It was found that a sulphuric acid of 66° B. (= sp. gr. 1.767), as directed in the article referred to, did not answer nearly so well as a stronger acid of sp. gr. 1.835. The amido group was eliminated by the same method which was used for the meta compound.

The comparison of the oxidation of the three nitro-toluenes was conducted as follows: About one gram of each nitro-toluene was boiled for three hours with a mixture of 25 grams of potassium ferricyanide, 10 grams of caustic potash, and 100 cc. of water. The unoxidised nitro-toluene was then distilled over in a current of steam. The solution was filtered and the filtrate evaporated till quite concentrated. When cold the potassium ferrocyanide which crystallised out was filtered off, and the crystals washed till the filtrate and washings amounted to 70 cc. The filtrate was acidified with 5 cc. of concentrated sulphuric acid diluted with an equal volume of water. It was then extracted three times with ether, using about 20 cc. each time. The ethereal extract was allowed to evaporate spontaneously in a weighed platinum dish, and the residue was dried over sulphuric acid till the weight was constant.

The residue obtained in this way by the oxidation of one gram of ortho-nitro-toluene was 0.69 gram; that obtained from one gram of para-nitro-toluene was 0.73 gram, while that obtained from one gram of meta-nitro-toluene was 0.052 gram. In another experiment with meta-nitro-toluene two grams were boiled for three hours with twice the amount of the oxidising mixture used above. The residue obtained weighed 0.087 gram, and 1.67 grams of unoxidised nitro-toluene were recovered.

Of course these numbers are no exact measure of the relative ease with which the three nitro-toluenes are oxidised. In the case of the meta compound the amount of the nitro-toluene in contact with the oxidising mixture must have been nearly the same from

[1] Berichte der deutschen chemischen Gesellschaft **17**, 263.

the beginning to the end of the experiment; with the ortho and para compounds, on the other hand, the nitro-toluene had nearly disappeared at the end of three hours. Further, the residues could not have been quite pure nitro-benzoic acid in either case, and the impurities would be likely to form a larger per cent. of the small amount of meta-nitro-benzoic acid than of the large amounts of the ortho and para acids. However, the experiments prove beyond question that while ortho and para-nitro-toluene are oxidised readily and in nearly equal amount by the mixture we are studying, meta-nitro-toluene is oxidised with great difficulty—with greater difficulty, indeed, than toluene itself.

In order to obtain enough of the meta-nitro-benzoic acid for analysis more than a dozen oxidations were made. In all, 400 grams of potassium ferricyanide were used. The acid obtained was converted into the barium salt. After two crystallisations the salt was nearly pure, the acid obtained from a portion of it fusing at 137°–138°. A small portion of the salt, after boiling with bone-black and recrystallising, gave an acid fusing at 140°–141°. The analyses were made with the less pure salt, but with three different sets of crystals. The salt used for the third analysis had stood a day longer than the others, and was probably slightly effloresced, as meta-nitro-benzoate of barium loses its water very easily.

The analyses were as follows:

I. 0.0613 gram of the salt lost 0.0080 gram H_2O at 150°.

II. 0.0584 gram of the salt lost 0.0076 gram H_2O at 150°, and gave 0.0245 gram $BaSO_4$.

III. 0.0629 gram of the salt lost 0.0080 gram H_2O at 150°, and gave 0.0271 gram $BaSO_4$.

	Calculated.	Found.		
		I.	II.	III.
Ba	25.32	...	24.68	25.34
$4H_2O$	13.31	13.05	13.01	12.72

If we take the same view of the conduct of meta-nitro-toluene, which has ordinarily been taken of the conduct of ortho compounds toward chromic acid, it would seem to follow that a nitro group in the meta position with reference to a methyl group protects the latter from oxidation by potassium ferricyanide and caustic potash. A consideration of the conduct of toluene and the brom-toluenes toward the same oxidising agent leads to a different conclusion.

Their conduct seems to indicate that it is not so much that a nitro group in the meta position *protects* a methyl group, as that a nitro group in the ortho or para position has, as it were, a *loosening* effect on a methyl group, causing the latter to be more easily attacked by the oxidising agent which we are studying. The sulphamide group in the para position seems to have much the same effect as the nitro group.

A somewhat similar effect of the nitro group has already been noticed by Körner.[1] He found that when a nitro group is in the ortho or para position with reference to a halogen atom, the latter can be easily exchanged for an amido or a hydroxyl group by boiling with alcoholic ammonia or potash. If the nitro group is in the meta position such an exchange cannot be effected by that means.

It seems probable from the results of the experiments described that we have discovered in potassium ferricyanide and caustic potash a means of oxidising a methyl group which is ortho to a nitro group, leaving a second methyl in the meta position untouched. Such an agent has been hitherto unknown.

University of Tennessee, *May 19th*, 1885.

ON BENZOYLACETIC ACID AND SOME OF ITS DERIVATIVES.[2]

Part I.

By W. H. Perkin, (Jun.), Ph. D., *Privatdocent at the University of Munich.*

Among the many methods which have been discovered and employed in the last few years, for the synthesis of organic compounds, those which are based on the use of acetoacetic ether are among the most important, this body being useful in two ways for building up organic bodies: in the first place, on account of the acid character of the hydrogen-atoms contained in the methylene-group; and in the second place, being a ketone, it is capable of entering into almost all the reactions which characterise the latter

[1] Jahresberichte, 1875, 365.

[2] Communicated by the Author.

class of bodies. The replacement of the hydrogen-atoms in aceto-acetic ether, by alcohol and acid radicals, has been especially studied by Wislicenus and his pupils; whereas the reactions which involve the ketone-group have, with few exceptions, been more or less neglected.

The reason of this is that not only are the experimental difficulties great, but there is also considerable uncertainty in interpreting the results, owing to the mobility of the different groups in aceto-acetic ether. More especially does doubt exist as to the part played by the methyl-group in such reactions and condensations. For this reason it appeared to me that it would be very interesting to carefully examine the benzoylacetic ether, recently discovered by Baeyer,[1] with especial reference to reactions in which the ketone-group takes part. Benzoylacetic ether, as was to be expected, gives in the aromatic series bodies exactly corresponding to those obtained from acetoacetic ether in the fatty series, and for this reason, as well as on account of the stability of the benzoyl-group, and the greater tendency of bodies in the aromatic series to crystallise, it seemed to be especially adapted to the study of the more complicated condensations.

Before entering into the details of this research, I should like to express my sincere thanks to Professor Baeyer, in whose laboratory it was carried out, for his kind help and advice which he always placed at my disposal during its progress, as well as for the interest which he took in all my other studies. I must also thank Herr C. Bernhart for the help which he gave me in the experimental part.

Part I of this research comprises the preparation and properties of benzoylacetic ether, benzoylacetic acid, and the compounds in which the hydrogen-atoms in the methylene-group are replaced by alcohol radicals.

Preparation of Phenylpropiolic Acid.

Cinnamic acid, as is well known, combines directly with two atoms of bromine, being thereby converted into phenyldibromo-propionic acid, thus:

$$C_6H_5.CH:CH.COOH + Br_2 = C_6H_5.CHBr.CHBr.COOH.$$

This acid, on treatment with alcoholic potash, first gives up 1

[1] Ber. **15**, 2705.

mol. of hydrobromic acid, forming the two isomeric *α*- and *β*-monobromocinnamic acids according to the equation—

$$2C_6H_5CHBr.CHBr.COOH = C_6H_5CBr:CH.COOH + C_6H_5CH:CBr.COOH + 2HBr.$$

α-Monobromocinnamic acid. *β*-Monobromocinnamic acid.

By converting these acids into ammonia salts and recrystallising once or twice from water, it is easy to separate the one from the other, the ammonia-salt of *α*-monobromocinnamic acid being much less soluble than that of the *β*-acid. Of these two bodies only the *α*-acid gives a good yield of phenylpropiolic acid on treatment with alcoholic potash, the *β*-acid being partly transformed into monobromostyrolene and other secondary products.[1] It is therefore necessary, before heating with potash, to transform the *β*-acid into the *α*-acid, which is easily done by heating it some degrees above its melting point, or more simply still by etherification, in which case the ether of the *α*-acid is formed. The formation of phenylpropiolic acid from *α*-monobromocinnamic acid is represented by the following equation:

$$C_6H_5.CBr:CH.COOH = C_6H_5.C\vdots C.COOH + HBr.$$

After many experiments, however, it was found that the following modification of the above process gives the best results, at the same time rendering the somewhat troublesome transformation of the *β*- into the *α*-monobromocinnamic acid unnecessary.

500 grams of cinnamic acid are suspended in about 1–1½ litres of absolute alcohol, and hydrochloric acid is passed through till the whole is dissolved and the liquid is thoroughly saturated with the gas. The product, after standing for two or three hours, in order to make sure that the reaction is complete, is poured into ice and water, and the oil which sinks to the bottom is separated by means of a tap funnel, the watery liquid being extracted with a little ether. This oil, which consists of almost pure cinnamic ether, is next dissolved in a little ether, washed with a dilute solution of sodium carbonate, to remove traces of hydrochloric acid and unchanged cinnamic acid; and after thoroughly drying over chloride of calcium, treated with 440 grams of bromine, in small quantities at a time, care being taken to keep the liquid cool. The bromine disappears instantly without evolution of hydrobromic acid. After

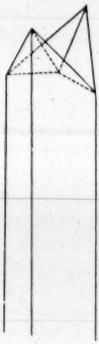
[1] Barisch, J. pr. Chem. [2], **20**, 180; Glaser, Annalen, **154**, 140.

standing for a short time, the whole is poured into a large open dish and the ether allowed to evaporate, when phenyldibromopropionic ether separates out in large crystals, forming a solid cake at the bottom of the dish. The crystals are then separated from the mother-liquor, pressed between filter-paper, exposed to the air for a short time to remove traces of bromine, and lastly, if necessary, crystallised from ligroin or alcohol.

The mother-liquor on evaporation deposits crystals of the ether, which are somewhat discolored by impurities, but on recrystallisation may easily be obtained pure, and melting at 69°.

A weighed quantity of this body is now added to the calculated quantity of alcoholic potash (1 mol. of ether requires 3 mols. of potash). The reaction is so energetic that the heat evolved is generally sufficient to cause the alcohol to boil. As soon as all the ether has been added, the whole is heated to boiling for six to eight hours in a flask connected with an inverted condenser. After distilling off the alcohol, the residue, which consists of a mixture of potassic phenylpropiolate and potassic bromide, is dissolved in water and filtered, and the clear liquid is acidulated with an excess of dilute sulphuric acid, which precipitates the phenylpropiolic acid as an oil, which, however, on standing, soon solidifies, especially if well agitated from time to time. The crude acid is next filtered off, well washed with water, dissolved in carbonate of soda solution, and gently heated with animal charcoal for about half an hour on a water-bath, agitating well from time to time. After filtering off the animal charcoal, an almost colorless solution of soda-salt is obtained, which, on acidulating with sulphuric acid, deposits the phenylpropiolic acid nearly pure. If required perfectly pure, it must be crystallised from water, and is thus easily obtained in well-characterised crystals, which Professor Haushofer was kind enough to measure and describe as follows :

Phenylpropiolic Acid.



"Prismatic crystals of the rhombic system with monoclinic habit. Acute dihedral angle of the prism 66° 50′. Of pyramidal faces, there appear constantly only the pair resting on an obtuse edge of the prism. Very characteristic is the twin-combination of the crystals according to the macropinacoid, whereby the hemi-

pyramids of the two individuals are symmetrically joined, and form re-entering angles. The entire development of the crystals is so decidedly monoclinic, that my reference of them to the rhombic system is based solely on the directions of extinction on the prismatic faces, which directions are exactly parallel and perpendicular to the prismatic edges."

Phenylpropiolic acid is produced from the dibromophenylpropionic ether according to the following equation:

$$C_6H_5.CHBr.CHBr.COOC_2H_5 + 3KOH = C_6H_5.C:C.COOK + 2KBr + 2OH_2.$$

By this method there is apparently no bromstyrolene formed, and if care be taken to avoid any large excess of potash in saponifying the dibromophenylpropionic ether, the yield is very good, about 80–85 per cent. of the theoretical amount. If, however, excess of potash be used, the phenylpropiolic acid is easily decomposed into phenylacetylene and acetophenone.

Preparation of Benzoylacetic Ether.

The phenylpropiolic acid must now be converted into the ethylic ether, which is best done in the following way. Pure phenylpropiolic acid is dissolved in absolute alcohol, and hydrochloric acid gas is passed through the liquid till the whole is thoroughly saturated, care being taken to cool the liquid well during the operation, after which the product is left at rest for two or three hours in order to complete the reaction. The whole is then poured into ice-cold water, and the phenylpropiolic ether, which is precipitated as an oil, is two or three times extracted with ether.

The etheric solution, after washing with dilute carbonate of soda, is well dried over chloride of calcium and the ether is distilled off, when pure phenylpropiolic ether remains behind as a thick, and almost colorless oil, having a fruity smell and burning taste; it does not solidify at 0°. If rubbed on the skin it produces a most painful burning sensation. When quickly distilled it boils between 260° and 270° without undergoing much decomposition. When this ether is dissolved in common sulphuric acid it takes up the elements of water, forming ethylic benzoylacetate, thus:

$$C_6H_5.C:C.COOC_2H_5 + H_2O = C_6H_5.CO.CH_2.COOC_2H_5.$$

For the formation of benzoylacetic ether in this way, commercial sulphuric acid is somewhat too concentrated, and a better yield is obtained if a few drops of water are added to every kilogram before use.

The method of preparation is the following: From 2 to 3 kilos. of sulphuric acid are cooled to 0° in a freezing mixture, and then 100 grams of phenylpropiolic ether are slowly added, drop by drop, so that the temperature never rises above + 3°, the whole being well shaken after each addition. The sulphuric acid becomes colored slightly brownish during the reaction, and there appears always to be a little sulphurous anhydride formed, especially if a rise of temperature takes place. After standing for two or three hours at as low a temperature as possible, the product is slowly poured on powdered ice, everything being carefully cooled, and the operation being best performed by allowing the sulphuric acid to trickle into a funnel filled with ice, which is kept well stirred all the time. The watery liquid, which is filled with drops of oil, is repeatedly extracted with ether. The etheric solution is then quickly washed with a dilute solution of sodium carbonate, and finally dried over potassium carbonate, which, as a rule, extracts a quantity of coloring matter. After filtering from potassium carbonate and distilling off the ether, crude benzoylacetic ether remains behind as a thick yellowish oil.

In order to purify this liquid, it is next shaken with a cold dilute solution of caustic soda and a little animal charcoal, and filtered, the whole operation being performed as quickly as possible, in order to avoid decomposition of the ether. The clear alkaline solution is next mixed with ice, acidulated with dilute sulphuric acid, and well shaken with ether; and lastly, this etheric solution is carefully dried over potassium carbonate, and the ether distilled off, when pure benzoylacetic ether remains behind as a colorless oil, which can easily be freed from traces of ether by leaving it for some time over sulphuric acid in a vacuum.

On analysis the following numbers were obtained:

I. 0.2072 gram substance gave 0.1198 OH_2 and 0.5208 CO_2.

Found.	Theory, $C_6H_5.CO.CH_2COOC_2H_5$.
C = 68.62 per cent.	68.75 per cent.
H = 6.42	6.25
O = 24.96	25.00

Benzoylacetic ether is a colorless oil having an agreeable smell, somewhat recalling that of acetoacetic ether. It does not solidify at 0°. If quickly fractioned most of it distils over between 265° and 270° without much decomposition. Under a pressure of 200 mm. it passes over between 230° and 235°. It should not, however, be distilled, if this operation can be avoided, as it entails considerable loss, and the crude ether is generally pure enough for most purposes.

Benzoylacetic ether is sparingly soluble in water, but mixes with ether and alcohol in all proportions. The solution in alcohol gives the same violet coloration with chloride of iron as acetoacetic ether. By boiling with water, or better with dilute sulphuric acid, it is split up into acetophenone, alcohol, and carbonic anhydride, according to the equation:

$$C_6H_5.CO.CH_2.COOC_2H_5 + H_2O = C_6H_5CO.CH_3 + CO_2 + C_2H_5OH.$$

This decomposition is exactly analogous to the splitting up of acetoacetic ether into acetone, alcohol, and carbonic anhydride. In benzoylacetic ether, just as in acetoacetic ether, the hydrogen-atoms in the CH_2-group are replaceable by sodium. It appears, however, that after having replaced 1 atom of hydrogen with sodium, it is necessary first to exchange this for some radical such as ethyl, before it is possible to insert another.

The sodium compound is best prepared by mixing benzoylacetic ether (4 grams) with a strong solution of sodium ethylate in alcohol, containing the calculated quantity of sodium (0.6 gram). The reaction takes place according to the equation:

$$C_6H_5.CO.CH_2.COOC_2H_5 + NaOC_2H_5 = C_6H_5.CO.CHNa.COOC_2H_5 + C_2H_5OH.$$

After standing for some time in the dark, the sodium-compound crystallises out in long silky needles, which, however, on being exposed to the air, quickly turn brown, especially when moist.

The mother-liquor is then drawn off by means of a vacuum pump, and the crystals are pressed between filter-paper, when the sodium-compound is obtained pure, having somewhat the appearance of cotton-wool. On standing in contact with the air, however, it slowly decomposes. If heated in the dry state it decomposes easily, yielding acetophenone and other bodies. It is readily soluble in water and alcohol, almost insoluble in ether.

The following derivatives of benzoylacetic ether were prepared by precipitation from a solution of the sodium-compound in water.

The *barium compound*, $(C_{11}H_{11}O_3)_2Ba$, is precipitated on adding barium acetate as a white amorphous mass, sparingly soluble in water, but more so in alcohol.

The *silver compound*, $C_{11}H_{11}AgO_3$, is formed by adding a solution of silver nitrate. It is a white amorphous precipitate. On warming, silver is immediately precipitated; it is also easily decomposed by caustic soda.

On adding copper sulphate to the solution of the sodium salt, the *copper compound*, $(C_{11}H_{11}O_3)_2Cu$, is precipitated as a pale green mass, insoluble in water. In dilute soda solution it dissolves easily, forming a beautiful blue solution, from which CuO is precipitated on boiling.

The *lead compound* is precipitated, on adding lead acetate, as a white precipitate, which is also soluble in caustic soda.

Ferric chloride gives a dirty violet coloration with dilute solutions of the sodium salt, the liquid becoming turbid on standing.

Benzoylacetic Acid.

Some time since Ceresole[1] by saponifying acetoacetic ether with dilute potash at ordinary temperatures, obtained the corresponding acetoacetic acid. It therefore appeared interesting to see if in this case, by saponification in the cold, benzoylacetic acid could be isolated, this appearing the more probable, as benzoylacetic ether is more stable than acetoacetic ether. Pure benzoylacetic ether was therefore dissolved in dilute aqueous potash ($2\frac{1}{2}$–3 per cent.), care being taken to avoid any large excess, and then left at rest at the ordinary temperature for about 24 hours. The product was then filtered, and after carefully cooling with ice, acidulated with dilute sulphuric acid, when the acid was precipitated in white flakes. After extracting with ether, the etheric solution was allowed to evaporate at the ordinary temperature, the acid remaining behind as a slightly brownish, hard, crystalline mass, which was next dissolved in dilute ammonia, shaken with a little animal charcoal, and filtered.

On acidulating with dilute sulphuric acid, and extracting with ether, the acid remained as an almost colorless crystalline mass, consisting of nearly pure benzoylacetic acid.

[1] Berichte **15**, 1871.

In order to obtain the body perfectly pure, it is dissolved in a little warm benzene (at 70°), and a trace of light petroleum added. On cooling, the acid crystallises out in small crystals, which, when seen under the microscope, appear in the form of thin transparent needles, which polarise light. The analysis gave the following numbers:

I. 0.1519 gram substance gave 0.0675 gram OH_2 and 0.3647 gram CO_2.

II. 0.1402 gram substance gave 0.0695 gram OH_2 and 0.3614 gram CO_2.

	Found.		Theory.
	I.	II.	$C_6H_5CO.CH_2.COOH$.
C =	65.48	66.06 per cent.	65.85 per cent.
H =	4.93	5.17	4.88
O =	29.59	28.77	29.27

Benzoylacetic acid, several times crystallised from benzene, melts at 103–104°, if quickly heated, at the same time undergoing decomposition, with evolution of carbonic anhydride. (The melting point, 85–90°, first given in the *Berichte* [16, 2129], is too low, owing to the fact that at that time I had not sufficient substance at my disposal to purify it by repeated crystallisation.)

The acid appears to sublime slowly at ordinary temperatures, so that if preserved in a test-tube, the sides, after some months, become covered with thin colorless transparent plates, consisting, apparently, of pure benzoylacetic acid. This acid is difficultly soluble in light petroleum, and crystallises from the hot solution on cooling in small flat needles. It is easily soluble in alcohol, ether and hot benzene. On adding light petroleum to the solution in benzene the acid is almost completely precipitated in the form of slender needles.

A small crystal of the acid dissolved in alcohol gives, on addition of a drop of ferric chloride, a beautiful reddish-violet coloration.

Benzoylacetic acid is sparingly soluble in cold water, the solution giving only a slight coloration on adding chloride of iron; it is much more easily soluble in hot water, a drop of chloride of iron producing an intense violet coloration.

Benzoylacetic acid may be formed directly, by dissolving finely powdered phenylpropiolic acid in concentrated sulphuric acid, according to the equation:

$$C_6H_5.C\vdots C.COOH + H_2O = C_6H_5.CO.CH_2.COOH.$$

When the acid liquid is poured on ice, a yellow amorphous mass is obtained, consisting of benzoylacetic acid, mixed with a little unchanged phenylpropiolic acid.

The former acid, on heating either alone or with dilute sulphuric acid, is quantitatively decomposed into acetophenone and carbonic anhydride, thus:

$$C_6H_5.CO.CH_2.COOH = C_6H_5.CO.CH_3 + CO_2.$$

The formation of acetophenone, by the action of concentrated potash on phenylpropiolic acid, is probably due to the latter first taking up the elements of water, being thereby converted into benzoylacetic acid, which is then decomposed by the further action of the alkali into potassium carbonate and acetophenone.

Benzoylacetic acid dissolves easily on shaking with dilute soda, sodium carbonate, or ammonia. In order to prepare the silver salt, the acid was dissolved in dilute ammonia, and the solution, after filtering, left over sulphuric acid in a vacuum till the excess of ammonia had volatilised, or, better still, carefully neutralised with pure nitric acid. On adding a solution of silver nitrate, the silver salt was precipitated in the form of a white amorphous mass, somewhat soluble in water. It was filtered off, well washed, and dried over sulphuric acid in a vacuum. The analysis gave the following numbers:

0.1440 gram substance gave 0.0567 gram silver.

Found.	Theory, $C_6H_5CO\,CH_2.COOAg$.
Ag = 39.37 per cent.	39.77 per cent.

The silver salt is instantly decomposed on heating, with separation of silver.

The following salts were prepared from the ammoniacal salt, which can be obtained as a waxy crystalline mass, by allowing the aqueous solution to evaporate to dryness in a vacuum over sulphuric acid. The crystals are generally mixed with traces of acetophenone, produced by the spontaneous decomposition of the salt. The ammonium salt is easily soluble in water. On adding *ferric chloride* to a solution of the ammonium salt, a thick blackish-violet precipitate is formed, which is slowly decomposed on boiling, carbonic anhydride being evolved. *Ferrous sulphate* does not give any precipitate. The *copper salt* is produced by adding a solution of copper sulphate to a fairly concentrated solution of the

ammonium salt, as a light greenish-yellow precipitate, which is not formed in dilute solutions. It is fairly stable, but is slowly decomposed on boiling.

The *lead salt* is precipitated, on adding acetate of lead, as a heavy white amorphous precipitate. The calcium and barium salts are easily soluble in water.

The salts of benzoylacetic acid are difficult to obtain pure and to analyse, on account of their tendency to decomposition into acetophenone and carbonic anhydride. From the above facts it is evident that benzoylacetic acid, although not a stable body, is much more so than acetoacetic acid, which has never been obtained pure enough for direct analysis.

Ethylbenzoylacetic Acid.

It was now necessary to see whether it was really possible, as in the case of acetoacetic ether, to replace the hydrogen atoms in the methylene-group, by alcohol-radicals, such as methyl, ethyl, etc., and thus to obtain higher homologues of benzoylacetic acid. The first experiment tried was the action of ethyl iodide on the sodium-compound of benzoylacetic ether, in the hope of getting ethylbenzoylacetic ether, according to the following equation:

$$C_6H_5.CO.CHNa.COOC_2H_5 + C_2H_5I = C_6H_5.CO.CH(C_2H_5).COOC_2H_5 + NaI$$

The method of procedure was the following:

0.6 gram of sodium was dissolved in about 15 cc. of absolute alcohol, and then mixed with 5 grams of pure benzoylacetic ether, taking care to avoid any rise of temperature. 10 grams of ethyl iodide were then added, and the whole heated on a water-bath till a sample, on dilution with water, had no longer an alkaline reaction. The alcohol and excess of ethyl iodide were then distilled off, the residue mixed with water, and the oily product extracted with ether. The etheric solution, after well washing and drying over carbonate of potash, left, on distilling off the ether, a thick yellowish oil, consisting probably of nearly pure ethylbenzoylacetic ether, which was, however, not further examined, as it appeared to be decomposed on distillation. In order to obtain the free acid, the oil was mixed with dilute alcoholic potash and left for several days at the ordinary temperature until, on diluting a sample with water,

only a small quantity of oil was precipitated. The product was mixed with water and several times extracted with ether, to remove any unchanged ethylic ethylbenzoylacetate. The solution of the potash salt of the new acid was then acidulated with dilute sulphuric acid, a solid acid being thereby precipitated, which was extracted with ether. After distilling off the ether, the acid remained behind as a semi-solid mass, which was first spread on a porous plate to remove traces of oil, and then purified by dissolving it in a small quantity of dilute alcohol, from which solvent it crystallises in small needles.

After drying at 60° the following numbers were obtained on analysis:

0.1914 gram substance gave 0.1082 H_2O and 0.4814 CO.

Found.	Theory, $C_6H_5CO \atop C_2H_5 > CH.COOH$.
C = 68.60 per cent.	68.75 per cent.
H = 6.28	6.25
O = 25.12	25.00

It was therefore ethylbenzoylacetic acid. The acid melts at 111–115° with slight decomposition, but could not be obtained free from traces of benzoic acid, which, while rendering it difficult to get an accurate melting point, do not much influence the analytical results. It is easily soluble in alcohol, ether, and benzene, and crystallises on evaporating the etheric solution in silky needles; it is easily soluble also in ammonia, soda, and sodium carbonate solution. When warmed with dilute sulphuric acid it is decomposed, carbonic acid being given off, and an oil remaining behind, probably consisting for the most part of ethylacetophenone.

Decomposition-products of Ethylbenzoylacetic Ether.

It next appeared interesting to determine whether the substituted benzoylacetic ethers would, on heating with alcoholic potash, undergo the same decompositions as the corresponding substituted acetoacetic ethers, which, as is well known from the researches of Wislicenus, are split up in two ways. He found, namely, that on employing a highly concentrated potash solution, the product consisted chiefly of organic acids, whereas with dilute solutions a large amount of ketone and only a small quantity of organic acids were obtained, according to the following equations, taking ethylacetoacetic ether as example:

I. $CH_3.CO.CH(C_2H_5).CO_2C_2H_5 + 2KOH = CH_3.CO_2K +$
$C_2H_5.CH_2CO_2K + C_2H_5OH.$
Butyric acid.

II. $CH_3.CO.CH(C_2H_5).CO_2C_2H_5 + 2KOH =$
$CH_3.CO.CH_2.C_2H_5 + C_2H_5OH + K_2CO_3.$
Methylpropyl ketone.

As will be seen from the following remarks, this rule applies also to the substituted benzoylacetic ethers.

In order to examine the decomposition-products of ethylbenzoylacetic ether, the crude ether was heated on a water-bath for three hours with moderately concentrated alcoholic potash. The mixture quickly became deep brown, and acquired a smell strongly resembling that of acetophenone. At the end of the reaction water was added, and the precipitated oil was separated from the potash-salt, by extraction with ether.

The etheric solution, after well washing with water, and drying with carbonate of potash, gave, on distilling off the ether, a dark brownish oil, which was then carefully fractioned. Almost the whole quantity distilled over by the first distillation, between 215–230°, and gave, on oft-repeated fractioning, an oil, boiling constantly at 220–222°.

The analysis gave the following results:

0.1588 gram substance gave 0.1140 gram H_2O and 0.4687 CO_2.

Found.	Theory, $C_6H_5.CO.CH_2.C_2H_5$.
C = 80.49 per cent.	81.08 per cent.
H = 7.97	8.10
O = 11.54	10.82

Propylphenylketone had therefore been formed from the ethylbenzoylacetic ether by splitting off CO_2 and alcohol, according to the following equation:

$C_6H_5.CO.CH(C_2H_5)COOC_2H_5 + 2KOH =$
$C_6H_5.CO.CH_2.C_2H_5 + C_2H_5OH + K_2CO_3.$

This ketone has already been described by Schmidt and Fieberg,[1] and by Burcker.[2] The former obtained it by the distillation of a mixture of benzoate and butyrate of lime, the latter by the action of aluminium chloride on butyric chloride and benzene.

[1] Ber. **6**, 498. [2] Bull. Soc. Chim. **37**, 4.

It does not combine with sodium bisulphite. On oxidation with chromic acid and sulphuric acid, benzoic and propionic acids are formed.

In order to examine the acids produced by the action of potash on ethylbenzoylacetic ether, the potassium salt which has been separated from the propylphenylketone, by extraction with ether, was next acidulated with dilute sulphuric acid, and distilled with steam. An almost colorless but strongly acid liquid distilled over, which possessed strongly the characteristic smell of butyric acid. The residue on cooling was extracted with ether.

On distilling off the ether a solid acid remained behind, which crystallised from water in silky plates, possessing all the properties of benzoic acid. They melted at 120°, and sublimed very easily on heating, and gave the characteristic iron reaction: in order to be certain the acid was turned into the silver salt and analysed with the following result:

0.4026 gram substance gave 0.1917 gram Ag = 47.59 per cent.
Theory for C_6H_5COOAg = 47.16

By the action of potash on ethylbenzoylacetic ether, a second decomposition had therefore taken place, according to the following equation:

$$C_6H_5CO.CH(C_2H_5).COOC_2H_5 + 2KOH = C_6H_5COOK + CH_3(C_2H_5).CO_2K + C_2H_5OH.$$

As in the case of substituted acetoacetic ethers, it was found on using very concentrated potash that mostly organic acids were formed, and that in order to get a good yield of phenylpropylketone it is advisable to use the alkali, moderately dilute, and to digest for a longer time.

Diethylbenzoylacetic Acid.

From the foregoing it is clear that one of the hydrogen-atoms in the methylene-group in benzoylacetic ether may be replaced by alcohol radicals, the result being the production of homologues of this ether, exactly corresponding in the aromatic series to the substituted acetoacetic ethers in the fatty series. It remained, however, to be tested whether the second hydrogen-atom could, in like manner, be replaced, *e. g.*, by ethyl, producing diethylbenzoylacetic ether. This, as a matter of fact, is the case. The experiment was carried out in the following way:

A mixture of 1.2 gram of sodium (dissolved in about 20 cc. of absolute alcohol), 10 grams benzoylacetic ether, and 10 grams ethyl iodide, was heated in a sealed tube for about three hours to 100°.

At the end of this time, the product having become neutral, the alcohol was distilled off, then 1.2 gram of sodium (dissolved as before in 20 cc. of absolute alcohol) added to the residue, and the whole was heated with 10 grams of ethyl iodide three or four hours to 100°.

The reaction takes place in two phases. In the first place, ethylbenzoylacetic ether is formed, which is then further acted on by the sodium ethylate and ethyl iodide, forming diethylbenzoylacetic ether, according to the following equation:

$$C_6H_5.CO.C(C_2H_5)Na.COOC_2H_5 + C_2H_5I = C_6H_5.CO.C(C_2H_5)_2.COOC_2H_5 + NaI.$$

At the end of the reaction the alcohol is distilled off, the residue diluted with water, and extracted several times with ether. After distilling off the ether the diethylbenzoylacetic ether remains behind as a thick dark-brown oil, which, as it could not be purified by distillation, was directly saponified and the acid examined.

For this purpose the ether was dissolved in alcohol, and after adding very dilute alcoholic potash, allowed to stand for some weeks at ordinary temperatures. The product was then diluted with water, and any unsaponified diethylbenzoylacetic ether removed by extracting several times with ether. On acidulating the solution of the potash salt with dilute sulphuric acid, an oily acid was precipitated, which, on standing for some time and continually stirring, became quite solid. It was once or twice extracted with ether, and the ethereal solution dried over calcium chloride. On distilling off the ether, diethylbenzoylacetic acid remained behind as a brownish crystalline mass, which was spread on a porous plate to remove traces of oil. The acid, which was now only slightly yellowish colored, was purified by dissolving in dilute ammonia and agitating with animal charcoal. On filtering and acidulating with dilute sulphuric acid, the acid was obtained in the form of an almost colorless crystalline solid. Although the saponification was conducted at ordinary temperatures, and with very dilute potash, the diethylbenzoylacetic acid always contained traces of benzoic acid, which spoilt the analytical numbers and melting point.

0.2121 gram substance gave 0.1325 gram H_2O and 0.5417 gram CO_2.

Found.	Theory $C_6H_5.CO.C.(C_2H_5)_2.COOH$.
C = 69.66 per cent.	70.90 per cent.
H = 6.94	7.27
O = 23.40	21.81

The acid melts at 128–130°. Heated either alone or with dilute sulphuric acid, it gives off carbonic anhydride, and an oil is left behind, probably diethylacetophenone.

Diethylbenzoylacetic acid is easily soluble in ammonia, soda, or sodic carbonate. On account of the difficulty of getting the acid pure, the salts were not further examined, it appearing probable that better results would be obtained on studying the decomposition-products of diethylbenzoylacetic ether.

Decomposition-products of Diethylbenzoylacetic Ether.

In order to examine these products, crude diethylbenzoylacetic ether was heated on a water-bath with dilute alcoholic potash for about five hours, by which means the ether was completely decomposed. After distilling off the alcohol and diluting with water, an oil was precipitated, which was separated from the solution of the potash salts by extracting with ether. The aqueous solutions were then gently warmed on a water-bath to get rid of the ether, acidulated with dilute sulphuric acid, and distilled in steam. A strongly acid, slightly turbid distillate came over, which smelt strongly of the higher members of the acetic series, and probably contained diethylacetic acid. The residue on cooling deposited an acid, in the form of feathery crystals, which were collected on a filter and washed with water. The acid crystallised from water in silky plates, which possessed all the properties of benzoic acid. They melted at 120°, and gave the characteristic reaction with ferric chloride. In order to be certain, the acid was turned into the ammonia salt and precipitated with silver nitrate. An analysis of the silver salt gave the following numbers:

0.2994 gram substance gave 0.1420 gram silver.

Found.	Theory C_6H_5COOAg.
Ag = 47.43 per cent.	47.16 per cent.

Diethylbenzoylacetic ether is therefore decomposed on heating with dilute alcoholic potash, partly into benzoic acid and diethylacetic acid, according to the equation:

$$C_6H_5.CO.C(C_2H_5)_2.COOC_2H_5 + 2KOH = C_6H_5.COOK + CH(C_2H_5)_2.CO_2K + C_2H_5OH.$$

The neutral oils, produced by the action of potash on diethylbenzoylacetic ether which had been separated from the potash salts by extraction with ether, were next examined. After drying over calcium chloride and distilling off the ether, a dark brownish oil remained behind, which was fractioned. The principal portion which distilled over between 220° and 235° gave, after several times carefully fractioning, an oil boiling constantly at 229–231° (at 710 mm.), which gave the following numbers on analysis, showing that diethylacetophenone had been formed:

0.1711 gram substance gave 0.1371 H_2O and 0.5099 gram CO_2.

	Found.	Theory $C_6H_5.CO.CH(C_2H_5)_2$.
C =	81.28 per cent.	81.81 per cent.
H =	8.90	9.09
O =	9.82	9.09

Diethylacetophenone is a thick colorless oil, which does not solidify at 0°, the smell of which closely resembles that of acetophenone. Bromine acts easily on the solution in glacial acetic acid, on warming, quantities of hydrobromic acid being given off. The product is a colorless oil, which was not further examined, as it could not be purified by distillation, owing to decomposition, and on standing for some weeks over sulphuric acid *in vacuo* it did not crystallise. The formation of diethylacetophenone by the action of potash on diethylbenzoylacetic ether may be expressed by the following equation:

$$C_6H_5.CO.CH(C_2H_5)_2.COOC_2H_5 + 2KOH = C_6H_5.CO.CH(C_2H_5)_2 + K_2CO_3 + C_2H_5OH.$$

Allylbenzoylacetic Acid.

This acid and its decomposition-products were more especially examined, on account of their isomerism with benzoyltetramethylene-carbonic acid and benzoyltetramethylene obtained by the action of trimethylene bromide on benzoylacetic ether (an account of which I hope to give in a short time), it being for several reasons interesting to determine any differences which might exist between these two bodies. Allylbenzoylacetic ether was prepared by the action of allyl iodide on the sodium compound of benzoylacetic ether in the following way:

10 grams of benzoylacetic ether were mixed with 1.2 gram of sodium (dissolved in about 15 cc. of absolute alcohol), and the whole, after adding an excess of allyl iodide, heated on a water-bath for about four hours, or better still in a sealed tube to 100° for two hours, after which the mass had acquired a neutral reaction. The alcohol was then distilled off, the residue diluted with water, and several times extracted with ether. After drying over chloride of calcium and distilling off the ether, allylbenzoylacetic ether remained behind as a thick brownish oil, which, as it could not be distilled without decomposition, was not directly analysed.

In order to obtain allylbenzoylacetic acid, the crude ether was dissolved in alcohol, a little dilute alcoholic potash added, and the whole allowed to stand at ordinary temperatures for three weeks. The product was then diluted with water, and any unsaponified ether removed by extraction with ether.

The solution of the potash salts was then acidulated with dilute sulphuric acid, and once or twice extracted with ether. After distilling off the ether, the acid remained behind as a brownish crystalline mass, which was first roughly purified by spreading out on a porous plate.

In this manner the acid was obtained as a yellowish crystalline mass, which was very easily soluble in most of the ordinary solvents, and for this reason could not be satisfactorily recrystallised from any of them. It was therefore dissolved in dilute ammonia, and after shaking with animal charcoal and filtering, reprecipitated and analysed with the following result:

0.1570 gram substance gave 0.0787 H_2O and 0.4005 CO_2.

Found.	Calculated, $C_6H_5.CO.CH(CH_2.CH:CH_2).CO_2H$.
C = 69.57 per cent.	70.58 per cent.
H = 5.57	5.78
O = 24.86	23.53

The acid always seems to contain traces of benzoic acid, which spoil the analytical numbers and melting point. It melted at 122–125°, and on further heating either alone or with dilute sulphuric acid, gave off carbonic anhydride and an oil, probably allylacetophenone. I hope later on, if possible, to find some other more suitable means of saponifying diethyl- and allyl-benzoylacetic ethers, and of thus obtaining the acids in a purer state.

Decomposition-products of Allylbenzoylacetic Ether.

The best proof of the formation of allylbenzoylacetic ether in the foregoing experiments was the study of its decomposition-products. In order to examine these, 10 grams of crude allylbenzoylacetic ether were heated for two or three hours with dilute alcoholic potash on a water-bath, by which means it was completely decomposed. After distilling off the alcohol, the residue was diluted with water, and in order to remove the neutral oils from the solution of the potassium salts, it was several times extracted with ether. The ethereal solution, after drying over calcium chloride and distilling off the ether, deposited 5 grams of a dark-brown oil, which was then fractioned.

The principal quantity distilled over between 230° and 240°, and gave on oft-repeated fractionation, an oil boiling constantly at 235–238° (at 710 mm. pressure), which on analysis gave numbers agreeing with those required for allylacetophenone.

0.1248 gram substance gave 0.0852 gram H_2O and 0.3757 CO_2.

	Found.	Theory, $C_6H_5.CO.CH_2.CH_2.CH:CH_2$.
C =	82.10 per cent.	82.50 per cent.
H =	7.58	7.50
O =	10.32	10.00

Allylacetophenone is formed by the action of alcoholic potash on allylbenzoylacetic ether according to the following equation:

$$C_6H_5.CO.CH(CH_2.CH:CH_2).CO_2C_2H_5 + 2KOH = C_6H_5.CO.CH_2.CH_2.CH:CH_2 + K_2CO_3 + C_2H_5OH.$$

Allylacetophenone is a colorless oil, boiling without decomposition at 235–238° (710 mm.).

It has a curious smell, something like that of camphor, and a burning taste. It is insoluble in water, but dissolves in most of the other solvents. It does not appear to combine with acid sodium sulphite.

The potash salts, which were separated from the allylacetophenone by extraction with ether, were evaporated nearly to dryness on a water-bath, acidulated with dilute sulphuric acid, and distilled in steam. The distillate, which had a strong acid reaction, was filled with drops of an unpleasantly smelling oil, which dissolved easily in a solution of sodium carbonate, and consisted probably of allylacetic acid.

The residue in the retort, on cooling, deposited a quantity of colorless crystals, which were filtered off and recrystallised from water. They then melted at 118–120°, gave with ferric chloride a reddish-brown precipitate, and showed all the properties of benzoic acid. It is therefore probable that part of the allylbenzoylacetic ether had been saponified by the action of the alcoholic potash into allylacetic acid, benzoic acid, and alcohol, according to the following equation :

$$C_6H_5.CO.CH(CH_2.CH:CH_2).CO_2C_2H_5 + 2KOH = C_6H_5CO_2K + CH_2:CH.CH_2.CH_2.CO_2K + C_2H_5OH.$$

Action of Bromine on Allylacetophenone.

Allylacetophenone being an unsaturated body, it appeared interesting to try the action of bromine on it, in the hope of obtaining a crystalline addition-product. The experiment was carried out in the following way :

Pure allylacetophenone was dissolved in glacial acetic acid, and after weighing the mixture, bromine slowly run in.

The color of the bromine disappeared instantly at first ; after a time, however, much more slowly, without the evolution of hydrobromic acid, the mixture becoming warm, rendering it necessary to cool the mass with water.

As soon as the color of the bromine was permanent, the whole was reweighed, when it was found that 1 mol. of allylacetophenone had taken up two atoms of bromine, according to the equation—

$$C_6H_5.CO.CH_2.CH_2.CH:CH_2 + Br_2 = C_6H_5.CO.CH_2.CH_2.CHBr.CH_2Br.$$

In order to isolate the product, the acid solution was poured into water, allylacetophenone dibromide being precipitated as a heavy oil, which was extracted with ether.

The ethereal solution was then washed once or twice with dilute sodic carbonate to remove any acetic acid, and finally dried over potassic carbonate. After distilling off the ether, a thick colorless oil remained behind, which, after standing over sulphuric acid *in vacuo* for 14 days, did not crystallise.

An analysis of this crude product gave the following numbers : 0.3180 gram substance gave 0.3812 gram $AgBr = 51.01$ per cent. Br. Theory for $C_6H_5.CO.CH_2.CH_2.CHBr.CH_2Br = 50.00$ per cent.

If the solution of allylacetophenone dibromide in glacial acetic acid be further treated with bromine, at the same time warming the mixture on a water-bath, the color of the mixture rapidly disappears, large quantities of hydrobromic acid being given off. In this experiment 4 grams of allylacetophenone dibromide, dissolved in glacial acetic acid, were treated with 1 gram of bromine, the whole being warmed on a water-bath till the reddish color had disappeared.

On pouring the liquid into water, an oil was precipitated which was extracted with ether.

After washing the ethereal solution with sodium carbonate and distilling off the ether, a thick oil remained behind, which, on standing for some days over sulphuric acid in a vacuum, deposited a quantity of crystals. These were roughly separated from the oily products by spreading them out on a porous plate, and finally once or twice recrystallised from dilute alcohol.

The analysis gave the following result:

0.4196 gram of substance gave 0.587 gram AgBr = 59.53 per cent. Br. Theory for $C_{11}H_{11}OBr_3$ = 60.15.

The substance was therefore bromallylacetophenone dibromide.

This body crystallises from dilute alcohol in four-sided prisms which melt at 121–122°.

It is easily soluble in alcohol, benzene, chloroform, ether, and carbon disulphide. In caustic soda it dissolves with a yellow color.

NOTES OF WORK FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA.

No. XIV.[1]

Communicated by W. G. Brown.

121.—ON A PLATINUM SILICIDE.

By C. G. Memminger.

In an attempt made to determine the amount of fluorine in a topaz from Stoneham, Maine, by volatilising the fluorine as silicon fluoride, a platinum silicide was formed in the following way.

[1] Nos. I-XIII appeared in the Chemical News, London, 1872–84.

A platinum crucible containing the powdered topaz was placed in a graphite crucible of such size that between the two crucibles a layer of "Jenning's" calcined magnesia (containing a trace of iron) of 7–10 mm. in thickness was packed, and the top of the graphite crucible carefully luted on with clay.

The crucibles were then placed in a powerful wind furnace fed with "retort carbon," and heated to the highest attainable temperature of the furnace—approximately the fusing point of wrought iron—for about two hours. After cooling, the graphite crucible was opened, and it was found that the platinum crucible had disappeared, and in its place were several metallic buttons mixed with the magnesia which had fritted together, and at the sides had combined with and was firmly attached to the graphite crucible.

The metallic buttons were freed from adhering earthy matters by alternate treatment with strong hydrochloric acid and solution of sodium carbonate.

Thus obtained, the nearly tin-white buttons were slightly attacked, and presented at first glance a frosted appearance; on closer examination it was noticed that on portions of the surface there were radiating straight lines more deeply etched, which were due to an irregular laminated structure.

The silicide is slightly malleable in the cold, but breaks after a few blows, showing a granular fracture, whiter than platinum, which under a pocket lens is seen to consist of the edges of the fractured laminæ intersecting at various angles, in some places giving the impression of an acicular aggregate. Before the blowpipe fusible in small pieces, or on the edges of a fracture. Hardness about 5. Specific gravity 18.97.

It dissolves with difficulty in aqua regia; the surface, during solution, becoming covered with a colorless layer of gelatinous silicic acid which impedes, then finally prevents the action of the solvent, and consequently has to be removed from time to time.

A qualitative analysis showed the presence in small quantity of other metals of the platinum group than platinum.

In the quantitative analysis after solution of the compound in aqua regia, the silica was separated in the usual way, and its purity tested by heating with a solution of pure sodium carbonate. There remained a little quartz sand and a few black scales which appeared to be graphite. The remaining constituents were determined in

the acid solution, but no attempt was made to separate the metals of the platinum group.

The analysis gave

				Ratio.
Platinum,	96.49	.4948		
Iron,	.78	.014	.5178	9.02
Magnesium,	.21	.009		
Silicon,	1.61	.0575	.0575	1.00
Quartz,	.51			
Undetermined,	.32			
	99.92			

Assuming the iron and magnesium to replace platinum, the formula is Pt_9Si, as above; but if the iron and magnesium are present as impurities the ratio is altered, giving nearly $Pt_{17}Si_2$.

The composition and mode of formation of this silicide varies from that of the few recorded, which may be briefly mentioned.

Berthollet[1] states that Descotils, by the method afterwards used by Boussingault (see below), obtained a button of platinum which was augmented in weight by .03; this augmentation in weight was at the time supposed to be due to carbon, but later experiments indicate that it was probably silicon. The button was very hard, easily broken, brilliant and lamellar in its interior.

Boussingault[2] obtained on heating platinum embedded in charcoal powder in a "creuset brasqué" a fused mass which had a specific gravity of 20.5. On heating strips of platinum embedded in charcoal powder he obtained what he called "platine cementé"; this had a specific gravity of 17.5–18. A silicide prepared by the first method was analysed. In this the amount of silicon was 0.5 per cent. or rather the platinum taken, 1 gram weighed after the experiment 1.005 gram. This silicide possessed essentially the same physical and chemical properties as the silicide which is the subject of this note.

Watts[3] mentions a silicide with 10 per cent. silicon, and one obtained by heating platinum with silicon in excess in the presence of cryolite which had the composition expressed by the formula $PtSi_6$, this is a white compound with gray crystalline fracture.

[1] Annales de Chimie et de Physique **67**, 88, 1808. [2] *Ibid.* **16**, 5 *et seq.*, 1821.
[3] Dictionary of Chemistry **4**, 672.

Boussingault[1] more than fifty years after his first experiments was led to repeat them, and states that the platinum increased in weight from 2.2–5.9 per cent. by its combination with silicon.

A. Colson[2] obtained compounds Pt_3Si and Pt_3Si_2, the latter with a specific gravity of 14.1.

The conditions under which the silicide, which is the subject of this notice, was formed are somewhat similar to those under which P. Schützenberger and A. Colson[3] made their experiments upon platinum silicide previously studied by the latter,[4] and their explanation that the silicon liberated—in this case, by the mutual action of the carbon and silica of the graphite crucible—was diffused in the condition of vapor, either as such or as they prefer, in combination with nitrogen or may be with nitrogen and oxygen, through the magnesia, seems to be more likely than the alternative that the silicon fluoride, driven off from the topaz, was decomposed by the platinum which combined with the silicon and liberated the fluorine. The latter point it is proposed to test experimentally.

122.—ANALYSIS OF A BERYL FROM AMELIA C. H., AMELIA CO., VIRGINIA.

By R. W. Baker.

Among the minerals, some of rare species, found at this locality,[5] are at least four varieties of beryl differing in color: a pale green in large crystals, a darker green in small well defined crystals, a translucent faint purplish or bluish white, and a transparent honey yellow variety. The two latter are frequently found together in the same crystal.

The beryl of which a portion was taken for analysis was a rough crystal, which in part was translucent white, the remainder transparent, varying in color from a wine yellow to a rich honey yellow. This last was separated and analysed. Vitreous to subadamantine lustre. Fracture subconchoidal. Specific gravity 2.702.

A thin section showed under the microscope many fluid inclusions, with and without movable bubbles, but no appearance of alteration or mineral inclusions.

[1] Comptes Rendus **82**, 591, 1876. [2] *Ibid.* **94**, 26, 1882. [3] *Ibid.* **94**, 1710, 1882.
[4] *Loc. cit.* [5] For list of minerals and occurrence see Am. Jour. Sci. III, **25**, May, 1883.

For the separation of the alumina, ferric oxide and glucina the method described by Genth[1] was used. The alumina and glucina after weighing were tested for glucina and alumina, but in neither case was either found to contain the other.

No other alkaline oxide than that of sodium was found, although the others were carefully tested for spectroscopically.

The loss on ignition is put down as water.

The results of the analysis and ratio of the constituents are as follows:

	I.			*a.*	*b.*	
SiO_2	65.24	1.087	1.087	6	7.25	29
Al_2O_3	17.05	.167	.181	1	1.21	5
Fe_2O_3	2.20	.014				
BeO	12.64	.506	.527	2.91	3.51	14
CaO	.57	.010				
Na_2O	.68	.011				
H_2O	2.70	.150	.150		1.00	4
	101.08					

Considering only the basic oxides and silica, it is seen in *a* that the formula obtained is that commonly received for beryl, $Be_3Al_2Si_6O_{18}$; but if the water is considered essential, as has been proposed by Penfield,[2] the ratio *b* could be written $H_8Be_{14}Al_{10}Si_{29}O_{92}$, which would give the calculated composition II.:

	II.	III.
SiO_2	65.11	65.24
Al_2O_3	19.09	18.45
BeO	13.10	13.14
H_2O	2.70	2.70
	100.00	99.53

This (II) agrees fairly well with the results of the analysis (III), gotten by replacing the ferric oxide, calcium monoxide and sodium oxide in I by the equivalent amounts of alumina and glucina.

The above formula differs considerably from that proposed by Penfield ($H_8Be_5Al_4Si_{11}O_{34}$), and its complexity without further evidence of its correctness is sufficient to prevent its acceptance. At the same time it should not be overlooked that both water and alkalies are probably normal constituents of beryl.

[1] Proceedings Am. Phil. Soc. Phila., **21**, 694. C. N., **51**, 86.

[2] Am. Jour Sci. (3), **28**, 25, 1884.

123.—ANALYSIS OF ALLANITE FROM NELSON CO., VIRGINIA.

By C. G. Memminger.

The locality at which this allanite was discovered is about three miles east of Lowesville, Nelson Co., Va. It is found in a vein at a depth of four to five feet from the surface of the ground, and, as far as it has been examined, the allanite is embedded in detached masses in the lower portion of or just below a "clay" formed by its weathering.

The masses of allanite are rounded, covered with a thin yellowish-white coating. On a surface of fracture the color is pitch black. Resinous lustre. Opaque. Uneven fracture with traces of cleavage. Streak greenish gray. Hardness 6. Specific gravity 3.59. Fuses before the blowpipe with intumescence. Easily decomposed by hydrochloric acid, with separation of gelatinous silica.

It gave on analysis:

SiO_2	30.04	.500	.500	1.97	6
SnO_2	.17	.001			
Al_2O_3	16.10	.158			
Ce_2O_3	11.61	.035			
Di_2O_3	5.39	.016	.254	1.00	3
La_2O_3	4.11	.013			
Fe_2O_3	5.06	.032			
FeO	9.89	.137			
MnO	tr.				
CaO	13.02	.233	.402	1.58	4.8
MgO	1.11	.028			
Na_2O	.28	.004			
K_2O	.02				
H_2O	2.56	.142	.142	.56	1.68
	99.36				

In calculating the ratios the atomic weights of cerium, didymium and lanthanum given by Meyer and Seubert were used, but the probability that the didymia was a mixture was not considered. The molecular ratio for the basic oxides and silica is greater than that now adopted for epidote, $RO : R_2O_3 : SiO_2 = 4 : 3 : 6$. Regarding the

water as non-essential, the formula is nearly $R''_5(R_2)^{vi}_3Si_6O_{28}$, or that of epidote in which the H is replaced by a metal, but if the water is essential the formula becomes $R''_5(R_2)^{vi}_3H_4Si_6O_{28}$. If in this formula and in the formula for epidote the hydrogen, or what amounts to the same, the water, is regarded as acidic, the oxygen ratio is 1 : 1.

124.—ON A DECOMPOSITION PRODUCT OF ALLANITE, A VARIETY OF KAOLINITE FROM NELSON CO., VIRGINIA.

By E. P. Valentine.

This substance is a product of the weathering of the allanite described in the preceding note. It is found in masses preserving the form and structure of that mineral: at times containing in the centre of the mass some unaltered allanite.

It is compact earthy. Breaks up in angular pieces. Brownish yellow, yellowish red to red in color. Adheres to the tongue. Not plastic. Crumbles readily between the fingers. Specific gravity in powder 2.606.

On charcoal blackens and becomes magnetic. With borax gives the reactions for iron. Heated in a closed tube gives off water having neutral reaction.

Decomposed by hydrochloric acid. Decomposed and partially dissolved on boiling with sodium hydroxide.

The particles of the crushed mineral under the microscope are transparent, of a wine yellow color. The powder is homogeneous, and between crossed Nicols shows no color.

The analysis of the air-dried mineral afforded:

				1	2
SiO_2	18.66	.311	.311		
Al_2O_3	23.28	.228			
Fe_2O_3	34.48	.215			
Ce_2O_3	1.30	.004	.459	1.5	3
La_2O_3	3.27	.010			
Di_2O_3	.65	.002			
MgO	.29	.007			
K_2O	.20	.002	.016		
Na_2O	.43	.007			
H_2O	17.16	.953	.953	3.06	6
	99.72				

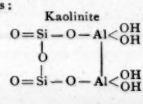
Giving the formula $(R_2)^{vi}_3H_{19}Si_3O_{19}$ in which, if the water is considered acidic, the ratio of basic oxygen to acidic 9:10 is nearly the same as that in the allanite from which this mineral is produced, 1:1. This is a change similar to that which takes place when beryl alters to kaolinite; there, if the water be considered acidic, the kaolinite retains the oxygen ratio of the beryl, ($Al_2H_4Si_2O_9$, 1:2). So too in this case there is a loss of protoxides with silica, while at the same time nearly all the rarer oxides have disappeared. There is another view which can be taken of its composition. It is kaolinite in which the two groups H_2O are replaced by two groups $(R_2)^{vi}(OH)_6$. Taking the formula for kaolinite $Al_2Si_2O_7 + 2H_2O$, that just found can be written $(R_2)^{vi}Si_2O_7 + 2[(R_2)^{vi}(OH)_6]$[1] where R_2 is Al_2, Fe_2, Ce_2, Di_2 and La_2. For this view can be cited the replacement of the water of halhydration of the crystallised sulphates of the iron group by an alkaline sulphate, *e. g.* $FeSO_4,H_2O + 6H_2O$ and $FeSO_4,(NH_4)_2SO_4 + 6H_2O$.

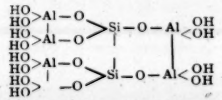
If this view be accepted, the compound, assuming its homogeneity, cannot be regarded as a species, and yet it differs sufficiently from kaolinite to have that difference indicated, but this in the present state of mineralogical nomenclature can only be done by adding another name to an already very long list in which species and variety have equal prominence.

This substance is only one of the products of the weathering of allanite. Another analysed by J. R. Santos[2] gave:

[1] These empirical formulæ may be written graphically, using Al to represent the pseudo-triads, thus:

Kaolinite





It is not intended by these "ingenious pictorial representations which are sometimes called the structural formulæ of mineral compounds," to convey the idea that this is the actual molecular composition and grouping of the elements, but only to indicate until means are at hand to determine the molecular formulæ of solids, that if it be permitted to assume the valence of elements in the gaseous state for the same elements in solids, that the second of these compounds can be represented as a derivative of the first, the first being a derivative of a metasilicic acid ($H_2Si_2O_5$), and that in both only the ordinarily accepted valences of silicon, aluminum and oxygen are used. Nothing more is intended by these formulæ than to represent a relation, such as is commonly done when sodium acetate is represented as a derivative of acetic acid, or perhaps as sodium acetate is related to silver acetate, or more generally whenever to a solid or liquid is assigned a formula which belongs demonstrably only to the gas.

[2] Chem. News **38**, 95, 1878.

SiO_2	21.37	.356	.356	1.04
Al_2O_3	20.66	.2025	.3396	1.00
Fe_2O_3	12.24	.0765		
Ce_2O_3	21.90	.0606		
BeO	1.95	.08		
H_2O	21.37	1.187	1.187	3.5
	99.49			

The formula found from this analysis $R_2SiO_5 + 3\frac{1}{2}H_2O$ is nearly that of miloschite $R_2SiO_5 + 3H_2O$. It will be seen in this analysis as in the preceding one that the ratio of Al_2O_3 to R_2O_3 is nearly 1 : 1.

125.—ANALYSIS OF A FIBROUS BI-SILICATE FROM NELSON CO., VIRGINIA.

By L. G. Patterson.

This mineral occurs interpenetrating the epidotic rocks in the axis of the Blue Ridge at Rockfish Gap Tunnel, Chesapeake and Ohio Railway, Nelson Co., Va.

It is found in the form of wedge-shaped fibrous massive layers, the fibres are parallel, in some specimens a decimetre long and not separable. Olive green to dark green color. Streak grey. Silky lustre. Brittle. Hardness 4. Specific gravity 3.153.

In the forceps fusible to a black glass. In the closed tube darkens, retaining its form. Not entirely decomposed by hydrochloric acid.

A thin section under the microscope appears to be quite fresh and without foreign admixture. It consists of parallel transparent elongated crystals of a light green color.

Its composition was found to be:

SiO_2	51.00	.850	.850	15.18
Al_2O_3	3.05	.029	.056	1.00
Fe_2O_3	4.35	.027		
FeO	12.83	.178	.757	13.51
MnO	.60	.008		
CaO	11.20	.200		
MgO	14.24	.356		
K_2O	.27	.003		
Na_2O	.73	.012		
H_2O	2.00	.111	.111	2.00
	100.27			

The ratio is fairly that of a bi-silicate, but whether pyroxene or amphibole was not determined.

126.—ON A CHLORITE FROM ALBEMARLE CO., VIRGINIA.

By M. Bird.

This mineral is not very abundantly found on Castle Mountain, in the Ragged Mountains about 4 miles south of Batesville, Albemarle Co., Va. It is there looked on as a "kind of soapstone," and it is prized on account of its softness as a material for the bowls of tobacco pipes.

It occurs massive, in small irregularly distributed scales, frequently in curved aggregations, giving the surface of fracture a rough granular appearance. Lustre of scales pearly, of mass glistening. Color olive green. Streak greyish green. Opaque to transparent in thin folia. Folia flexible, not elastic. In powder feels greasy. Tough. Hardness 2.5. Specific gravity 3.05.

In closed tube gives off water and turns black, but the shape of the fragment remains unchanged. Fuses readily to a black glass. On charcoal becomes magnetic. Decomposed by hydrochloric acid with the separation of pulverulent silica.

A thin section under the microscope shows the scales in groups of various forms, fan-shaped, sheaf-like, parallel, lentiform, with a little hydrated ferric oxide between the edges of the groups, otherwise the section appeared homogeneous. Pleochroic.

Analysis afforded:

SiO_2	23.52	.392	.392	1.697	5
Al_2O_3	22.35	.219	.231	1.00	3
Fe_2O_3	1.92	.012			
FeO	28.78	.399	.680	2.944	9
MnO	.32	.0045			
CaO	.39	.0069			
MgO	10.79	.2698			
H_2O	11.28	.626	.626	2.71	8
	99.35				

Giving the formula $R''_5(R_2)^{vi}_3Si_5O_{28} + 8H_2O$ in which the oxygen ratio of R'', $(R_2)^{v}$, Si, $H_2 = 9:9:10:8$ or nearly that of corundophilite as given by Dana[1] $1:1:1:\frac{5}{8}$.

In physical characters it appears to resemble more nearly thuringite, in which the oxygen ratio of the basic oxides to that of the silica and water is the same as in the mineral described, *i. e.* 1:1.

University of Virginia, *August 18th*, 1885.

[1] A System of Mineralogy, 5th Ed. p. 504.

ON THE DECOMPOSITION OF CINCHONINE BY SODIUM ETHYLATE.

By Arthur Michael.

The first step to an insight into the constitution of the quinine alkaloids was made by Gerhardt,[1] who found that a basic product is formed when quinine and cinchonine are distilled with caustic alkalis, which he called quinoline. The reaction is, however, by no means of so simple a nature as was supposed by the eminent French chemist, for, several years later, it was shown by C. G. Williams that cinchonine yielded, in this process, quite a number of decomposition products. Williams[2] succeeded in isolating from the basic product, besides quinoline, small quantities of pyrrhol bases, several pyridine bases, lepidine and higher boiling homologues belonging to the same series. We are also indebted to Williams[3] for an examination of the higher boiling products, when he obtained from the basic oil boiling above 280°, by a series of fractional distillations and precipitations with platinum chloride, homologues of quinoline up to a compound containing sixteen atoms of carbon. In this paper he conjectured that a base exists among the products of decomposition with the same number of atoms of carbon as are contained in cinchonine. This subject was not exhausted by Williams, as Oechsner[4] has lately shown that reduced quinoline bases are formed, and also that collidine from cinchonine consists of two isomers. Besides basic products, the formation of certain fatty acids has been proven by Lubawin.[5]

In all these investigations the method used was to distil a mixture of the alkaloid and caustic alkali, and examine the products of distillation. It is evident that these compounds may represent but a secondary stage of the reaction, as the alkaloid was exposed to a high temperature and to the energetic action of caustic alkalis. To obviate this, Wischnegradsky and Butlerow[6] have examined the reaction under different conditions, which they unfortunately have not described in their papers.[7] From quinine,

[1] Ann. Chim. et Phys. (III), **7**, 251.
[2] Chem. Gaz., 1855, 301.
[3] Laboratory, 1867, 109.
[4] Ann. Chim. et Phys. (V), 27.
[5] Berichte 1879, 1254.
[6] *Ibid.*, 1878, 1254; 1879, 1480, 2093.
[7] I have not been able to find it described, and have examined all the chemical journals with the exception of the Russian, which were not at my command.

a mixture of $C_{10}H_9NO$ (oxylepidine), ethylpyridine and fatty acids; from cinchonine, quinoline, ethylpyridine and fatty acids were obtained. Basing his speculations on these results, Wischnegradsky[1] suggested that cinchonine contains a reduced pyridine and quinoline group, held together by a propyl radical. These results are certainly in opposition to those of previous investigators; as there is no reason for supposing that the higher boiling bases examined by Williams and Oechsner are formed by distilling quinoline or lepidine with alkalis, and it is a matter of regret that the Russian chemists have not seen fit to publish the method by which they obtained such results.

Another hypothesis on the constitution of cinchonine was suggested by Koenigs,[2] who surmised that it consists of a quinoline and a reduced quinoline group, and that the ethylpyridine formation was due to the action of the alkalis on one of these groups. Somewhat later, judging from the analogous behavior of the carboxyl derivatives of pyridine and cinchene, Koenigs considered it possible that cinchonine contains a reduced pyridine group.

Among the researches on the oxidation of cinchonine may be mentioned, as bearing indirectly on our subject, that of Weidel and Hazura,[3] who have shown that the distillation of the syrupy product obtained in oxidising the alkaloid with potassium permanganate with zinc dust gave ethylpyridine; and that of Comstock and Koenigs,[4] who have isolated from the same oil, by means of bromine, tribromoxylepidine.

In taking up the study of the action of alkalis on the natural alkaloids I have been guided by the following reasons: It seemed to me that the decomposition of the alkaloid should be effected at a moderate temperature, if the primary products of the reaction are to be isolated; and, furthermore, the subsequent action of the alkali should be avoided as much as possible. These conditions are best realised by allowing the alkali and alkaloid to react in solution, by which an intimate contact is insured, and the dilution of the alkali at the same time lessening the likelihood of it acting as a reducing and oxidising agent. My experiments began with heating an alcoholic solution of sodium hydrate and cinchonine in an open vessel connected with reverse cooler. Under these conditions even continued heating for several days caused no apparent

[1] Berichte 1881, 2310.
[2] *Ibid.* 1881, 1852.
[3] Monatsheft für Chemie, 1882, 787.
[4] Berichte 1884, 1990.

decomposition, but when this solution was brought into a closed tube and heated to 100° a decided reaction was noticeable. After making a large number of experiments on the proper proportions and temperature, it was found that heating a solution of six grams of sodium hydrate in 60 cc. of absolute alcohol and six grams of powdered cinchonine[1] to 130–135° for 8 to 10 hours gave the most satisfactory results; since, when the amount of alcohol was decreased all the cinchonine did not go into solution and eluded decomposition, and heating to a higher temperature, even for a much shorter time, caused the tubes to open under pressure. The greater number of the tubes, when prepared and treated as described, opened without pressure; some, however, under a slight evolution of an inflammable gas.

The contents of the tubes were brought into a flask connected with a condenser, and the alcohol expelled by heating for a long time in a water-bath; the thick residue was then added to a large quantity of water, and the mixture extracted several times with ether. After distilling off the ether the residue was treated with steam, as long as the distillate had an odor.

The aqueous distillate was at no time turbid, although in the beginning of the operation it had quite a strong odor, resembling that of quinoline. A quantity of this distillate, obtained from the decomposition product of 250 grams of cinchonine—the basic products weighed over 200 grams—was extracted with ether, dried over $CaCl_2$, and, after evaporating the ether, subjected to a fractional distillation; but the small amount obtained, about three grams, did not permit a separation of the several products contained in it. About one-half a gram passed over under 65°; a larger quantity, one and one-half grams, between 100° and 200°, when the thermometer rose rapidly to 250° to 260°, at which temperature about one-half a gram distilled, leaving a small quantity in the flask. The lowest boiling fraction had the odor of pyridine, while the higher boiling portions had a decided quinoline odor. It was thought possible that part of the lower boiling products had gone over with the ether used in extraction; but on shaking it out with acidulated water, and evaporating the latter to dryness, only a very small residue was left.

As the bases obtained in treating with steam undoubtedly

[1] The cinchonine used in the first series of experiments contained a small percentage of cinchotine.

contained all the pyrrhol, pyridine and simpler quinoline derivatives formed in decomposing the alkaloid under the above-stated conditions, and hardly more than one per cent. of such products are formed, it is evident that these products represent a secondary reaction—probably an action of the alkali on the primary product. This result is very noticeably different from that obtained in decomposing according to the Gerhardt method, when the greater part of the distillate is composed of such products.

The basic product remaining in the flask after treating with steam was extracted with ether, the extract dried over calcium chloride and the ether evaporated. This left a viscous heavy oil of a reddish color. An attempt to purify this product by distillation at ordinary pressure showed that it decomposed into numerous products; in fact, it acted exactly like cinchonine does when distilled with alkalis; and the products obtained were, without doubt, those formed in the Gerhardt reaction. It seemed possible that distillation *in vacuo* would give a more satisfactory result, and 15 grams of crude base were fractioned under about 6 inches pressure at first, but the gaseous products formed soon drove the mercury column down to indicate about 12 inches pressure. The thermometer rose very rapidly to 300°, about 3 grams; more gradually to 360°, about 6 grams; and the residue, on cooling, solidified to a hard resinous mass. An attempt to purify these fractions by further distillation *in vacuo* showed that they decomposed into a series of lower boiling products. That, however, these products are not contained in the original product was shown by the fact that after several distillations the greater part of these products passed over very readily with steam. The resinous product remaining in the flask, when distilled under ordinary pressure, gave a series of lower boiling products.[1]

These experiments showed the improbability of purifying the product by distillation, and resort was taken to fractional precipitation with platinum chloride; a method which, as stated above, yielded good results in separating the higher boiling bases formed in the Gerhardt reaction. For this purpose it was necessary to start with pure cinchonine, and the alkaloid used in the following

[1] The crude basic product obtained from pure cinchonine appeared to act somewhat different on distillation *in vacuo*. About one-half passed over between 330° and 350°. On redistilling this portion *in vacuo* about one-half passed over under 335°, when about one-third passed over between 335° and 340°. A thermometer placed in the crude base could be heated to 300° without a perceptible quantity of base passing over.

experiments was purified by crystallising the commercial sulphate several times from water, then converting it into the acid sulphate and crystallising this seven times from alcohol, and a final crystallisation of the free base from the same solvent. It was found to be free of cinchotine. The alkaloid was decomposed in the manner described above, and about six grams of the base were dissolved in large excess of hydrochloric acid, filtered from a dark resin which seemed to be formed by the continued treatment of the base with steam, and the solution heated with bone-black, in a flask connected with a cooler, the operation was repeated until another treatment caused no further discoloration. The chlorhydrate was precipitated by adding successively twice 10 cc. of $PtCl_4$ solution (10 per cent.), and three times 15 cc. of the same solution. The first precipitate had a deep reddish-yellow color, the following to the fifth were colored orange, differing from each other but little in intensity, while the fifth had a decidedly deeper tint. All the precipitates of the platinum double salt had the same appearance under the microscope, consisting of round globular plates.

For analysis they were dried at first *in vacuo*, and then at 100° *in vacuo*. They could then be heated to 125° without causing any further loss in weight. It is necessary to dry the double salt *in vacuo* before heating it to 100°, as, when heated at once to that temperature, it melts under the water given off. The precipitates are numbered in the order of their precipitation.

I. 0.4353 gram of precipitate 2 gave 0.5486 gram of CO_2 and 0.1465 gram of H_2O.

II. 0.3186 gram of precipitate 3 gave 0.3972 gram of CO_2 and 0.1175 gram of H_2O.

III. 0.3166 gram of precipitate 4 gave 0.3671 gram of CO_2 and 0.1200 gram of H_2O.

IV. 0.2958 gram of precipitate 5 gave 0.3692 gram of CO_2 and 0.1075 gram of H_2O.

	Found.			
	I.	II.	III.	IV.
C	34.38	34.00	34.23	34.04
H	3.74	4.12	4.22	4.04

A second portion of the base (15 grams), obtained in a subsequent operation, was treated in a like manner, and precipitated by addition of equal weights of platinum chloride. The analyses of the salts, dried at 120°, gave the following results :

I. 0.6480 gram of first precipitate gave 0.1822 gram of Pt.

II. 0.3508 gram of second precipitate gave 0.4394 gram of CO_2 and 0.1310 gram of H_2O.

0.3595 gram of second precipitate gave 0.0984 gram of Pt.

0.4621 gram of second precipitate gave 15.2 cc. of N at 29.5° C. and 763 mm.

III. 0.3138 gram of third precipitate gave 0.3966 gram of CO_2 and 0.1146 gram of H_2O.

0.3529 gram of third precipitate gave 0.0963 gram of Pt.

0.4288 gram of third precipitate gave 0.1183 gram of Pt.

IV. 0.3644 gram of fourth precipitate gave 0.4600 gram of CO_2 and 0.1380 gram of H_2O.

0.3431 gram of fourth precipitate gave 0.0934 gram of Pt.

0.2702 gram of fourth precipitate gave 9.6 cc. of N at 30° C. and 762.3.

V. 0.3683 gram of fifth precipitate gave 0.4563 gram of CO_2 and 0.1270 gram of H_2O.

0.4523 gram of fifth precipitate gave 0.1241 gram of Pt.

	Found.					Theory for
	I.	II.	III.	IV.	V.	$C_{20}H_{26}N_2PtCl_4$.
C		34.13	34.46	34.42	33.90	34.12
H		4.15	4.10	4.20	3.93	3.98
N		4.10		4.41		3.98
Pt	26.56	27.37	27.29 27.59	27.22	27.39	27.69

The consideration of these analytical results leads to the conclusion that the basic product remaining after treating with steam is practically homogeneous; it containing but a small quantity of foreign bases, which caused the difference between the color of the first precipitate of double platinum salt and the subsequent precipitates, and showed itself in the percentage of platinum contained in the first precipitate.

The base $C_{20}H_{26}N_2$ is a heavy, reddish-yellow, viscous oil, and has, when cold, so great a consistency that it cannot be poured from the vessel containing it; on heating it becomes mobile. It has a faint odor, resembling slightly that of quinoline; the odor becomes stronger when the base is heated. Acids dissolve it to form the corresponding salts, which, as far as yet examined, are amorphous. On heating to boiling the base is decomposed into a number of lower boiling bases, probably derivatives of pyridine and quinoline. A solution of the chlorhydrate shows the following reactions:

$SnCl_2$, an amorphous yellowish precipitate.

$HgCl_2$, white amorphous precipitate, but slightly soluble in water.

$K_4Fe(Cn)_6$, pinkish precipitate with the appearance of crystalline structure. Soluble in hot water, but on boiling a precipitate is formed that causes the solution to take a bluish-green fluorescence.

$HgNO_3$, copious yellowish precipitate, which is difficultly soluble in boiling water.

K_2CrO_4, amorphous yellow precipitate, that dissolves in hot water, and separates out on cooling.

$K_3Fe(Cn)_6$, yellowish precipitate, soluble in boiling water.

The symbol $C_{20}H_{26}N_2$ stands in a very simple relation to that of cinchonine, which may be represented by the following equation:

$$C_{19}H_{22}N_2O + C_2H_5ONa = C_{18}H_{21}N_2(C_2H_5) + HCOONa.$$

This equation presupposes the existence of an ethyl in the base, which must be derived from the sodium ethylate used in the decomposition, and also the formation of formic acid. Although the examination of the alkaline solution remaining after extracting the base $C_{20}H_{26}N_2$ with ether has not been, from want of time, thoroughly examined, it is probable that it contained formic acid. The alkaline solution was acidulated with sulphuric acid, and treated with steam as long as the distillate showed an acid reaction. The distillate was carefully neutralised with sodium hydrate, and then evaporated to incipient dryness, when it solidified to a white crystalline mass. An aqueous solution of this salt gave on addition of silver nitrate and boiling, a mirror of reduced silver, which is a strong indication of the presence of formic acid.

The experiments described in this note make it very probable that the primary action of alkalis on cinchonine is analogous to that of sodium ethylate, forming the base $C_{18}H_{22}N_2$ and an alkaline formate; and that the bases obtained by previous investigators were due to the decomposition of this base by heat, or by the subsequent action of the alkali. At all events they make the constitution of cinchonine suggested by Wischnegradsky extremely improbable.

If the acid obtained in the above-described decomposition of cinchonine be formic acid, then it would appear that the alkaloid contains a formyl which is easily replaceable; a relation which suggests that cinchonine is an amide of the base $C_{18}H_{22}N_2$ and

formic acid.[1] It seems to me that the above experiments suggest a line of research which will prove very fruitful in the investigation of the natural alkaloids. An experiment with quinine showed that it undergoes a similar decomposition, which makes it probable that all alkaloids yielding quinoline will give analogous results. It is probable that the action of aqueous or dilute alcoholic alkaline solutions on cinchonine will yield the primary product of decomposition; and that a careful investigation of the base described above will throw some light on its constitution. These, and other researches suggested by the above experiments—as well as an examination of the therapeutic properties of the new compounds—will form the subjects of further investigations.

TUFTS COLLEGE, MASS., *July* 6, 1885.

ON SIMULTANEOUS OXIDATION AND REDUCTION BY MEANS OF HYDROCYANIC ACID.

BY ARTHUR MICHAEL AND GEORGE M. PALMER.

It seems to be generally acknowledged that the class of substances playing what is called a catalytic function in chemical reactions undergo some change during the process, although in the end they return to their original form; and the name commonly given implies but an imperfect understanding of this function. It is probable that many of the most important reactions of animal and vegetable life are due to the intercession of such substances. Some of these reactions seem to be dependent on substances capable of decomposing water into its elements, or into hydrogen and hydroxyl; and, when the chemist can command a reagent possessing that property at a low temperature, their imitation in the laboratory may closely follow its discovery.

A substance which is endowed with the property of causing

[1] I was about to make some experiments on the action of sodium ethylate on amides when I received the June number of the Berichte, which contained a paper by R. Seifert (1885, 1355) on the same subject. This chemist shows that sodium ethylate acts on acetanilide and acetamide, forming ethylaniline and ethylamine. It is evident that these reactions are perfectly analogous to that of sodium ethylate on cinchonine.

water to react on certain organic bodies, and apparently at the same time remaining unchanged, is hydrocyanic acid; although as yet the reactions in which this is known are but few. The first reaction where hydrocyanic acid was used for this purpose was investigated by Strecker,[1] who showed that alloxan, in the presence of ammonia, decomposes hydrocyanic acid into dialuric acid and oxaluramide; and that not only a small quantity of acid causes a considerable amount of alloxan to decompose, but the decomposition proceeds in the cold. In this paper Strecker made the ingenious surmise that the poisonous properties of hydrocyanic acid may be due to a similar action on the constituents of blood. To the same category of reactions belong the interesting observations of Wallach[2] on the formation of dechloracetic acid, or ether, by the action of HCn on aqueous, or alcoholic, chloralhydrate; and also that of Böttinger,[3] who obtained lactic and carbonic acids in the action of hydrocyanic and hydrochloric acids on pyruvic acid. The same chemist[4] investigated the behavior of glyoxylic acid towards nascent hydrocyanic acid, and found it is decomposed into glycolic and oxalic acids.

We have undertaken a systematic investigation of the action of hydrocyanic acid, in the presence of water or alcohol, on substances easily susceptible of reduction or oxidation, and hope to ascertain the laws governing its action on such substances. In the present paper will be found the results obtained in the investigation of a number of aromatic compounds.

Action of Alcoholic Hydrocyanic Acid on Benzile.

This reaction has been investigated by Zinin,[5] who obtained an addition-product of one molecule of benzile and two of hydrocyanic acid; and, lately, the compound has been converted into the amide of an acid.[6] This behavior of benzile towards hydrocyanic acid only takes place when the directions of Zinin are closely followed, as under slightly different conditions quite another result is obtained. We tried, at first, the action of nascent hydrocyanic acid according to the method discovered by Urech. For this purpose 10 grams of benzile and 7.5 grams of pure KCN were mixed, 100 cc. of absolute alcohol added, and

[1] Annalen **113**, 47.
[2] Annalen **188**, 328.
[3] Annalen **34**, 189.
[4] Berichte, 1877, 1084.
[5] Berichte Annalen **173**, 288.
[6] Burton, Berichte, 1883, 2232; also Japp and Miller, *ibid.* 1883, 2418.

the mixture heated until the benzile was dissolved. To the moderately warm solution 10 grams of strong hydrochloric acid (saturated at 8°) were added, drop by drop, and the solution constantly shaken during the operation. The solution, which was reddish brown before adding the acid, became colorless. As much of the alcohol as possible was then expelled, the residue extracted with ether, the ethereal solution separated, and the ether driven off. The residual oil was then shaken with a strong solution of sodium hydrogen sulphite, allowed to stand for some time, and extracted with ether. On evaporation of the ether an oil remained, which was fractionated. The bulk was found to pass over between 205°–208°, and on a second fractionation between 206°–207°. This oil was ethyl benzoate; as was shown by its physical properties, and by boiling with caustic potash, when it was decomposed into potassium benzoate and ethyl alcohol. From the sulphite solution pearly crystalline plates had separated; these were the double salt of acid sodium sulphite and benzaldehyde. On adding sufficient sodium carbonate to make the solution alkaline, and boiling, an oil passed over, which boiled at 180°, and was converted into benzoic acid by treating with nitric acid. The amount of ethyl benzoate and benzaldehyde obtained was greater than that of the benzile used.

It is evident from these results that benzile is decomposed by nascent hydrocyanic acid and alcohol quantitatively according to the following equation:

$$C_6H_5COCOC_6H_5 + C_2H_5OH + HCN = C_6H_5-COOC_2H_5 + C_6H_5CHO + HCN.^1$$

It became of interest to ascertain whether free hydrocyanic acid would cause the decomposition of benzile, and a tube containing twenty grams of benzile, absolute alcohol, and a few cc. of strong hydrocyanic acid was heated at 200° for four hours. The contents of the tube were heated until the alcohol was driven off, water added, then shaken out with ether, and the ethereal solution fractionated. Between 160°–190° benzoic aldehyde passed over—this was proved by forming the addition-product with sodium hydrogen sulphite, and oxidation to benzoic acid—between 190°–210° an oil, which on re-

[1] Benzile undergoes, according to Jourdan (Berichte, 1883, 658), the same decomposition when exposed to the action of alcohol and potassium cyanide. It does not seem improbable that the decomposition is due to the presence of a small quantity of free hydrocyanic acid.

distilling passed over almost completely from 204°–207°. This fraction consisted of benzoic ether. Above 210° the thermometer rose rapidly to 250°, when between that temperature and 300° a solid substance distilled. This substance consisted of rectangular plates, and was shown to be benzoic acid. It is evident that hydrocyanic acid in a free state possesses equally with the nascent acid the property of decomposing benzile by causing the addition of the elements of alcohol.

Although it seemed very improbable that alcohol alone would decompose benzile, the experiment was made. It was found that benzile and alcohol could be heated together in a closed tube to 200° without the benzile being in the least decomposed.

Action of Hydrocyanic Acid on Benzoquinone.

According to Levy and Schultz[1] anhydrous hydrocyanic acid is without action on benzoquinone; this is, however, not the case when the nascent acid is used. Six grams of quinone were dissolved in absolute alcohol, five grams of pure potassium cyanide added—the solution turned dark and warmed perceptibly, indicating that the salt itself reacts on benzoquinone—and eight grams of hydrochloric acid (spec. grav. 1.22) were slowly added to the cold solution. The mixture was allowed to stand for twenty hours, then the alcohol distilled off, water added to the residue and treated with steam. The liquid remaining after treatment with steam was extracted with ether, which dissolved a black crystalline mass. This was pressed between bibulous paper and carefully sublimed. By crystallising this product we obtained long hexagonal prisms, melting at 168°–169° and having all the properties of hydrobenzoquinone. The distillate obtained by treating with steam was extracted with ether, and on evaporation of the solvent, a small quantity of an oil remained. This oil has the odor of guaiacol, and was, perhaps, ethylhydrobenzoquinone.

The reaction has not been sufficiently examined to give a clear insight into its nature, although the reducing power of hydrocyanic acid is very apparent. It seems not unlikely that an examination of the oil, or a more minute investigation of the products formed than was permitted with the small quantity of quinone used in the above experiment, will show the manner in which the oxygen is employed. We shall repeat the experiment on a larger scale.

[1] Annalen der Chemie **210**, 143.

Action of Alcoholic Hydrocyanic Acid on Benzoïn.

The study of the action of hydrocyanic acid on benzoïn presented a peculiar interest in view of the formation of the compound from benzoic aldehyde by means of potassium cyanide. If hydrocyanic acid shows in this instance the property of decomposing benzoïn, we should be in possession of a reagent which would enable us to form retrogressively the aldehyde from its carbon-polymer.

Ten grams benzoïn dissolved in absolute alcohol and a small quantity of hydrocyanic acid were heated in a sealed tube at 200° for five hours. The contents of the tube were heated until the alcohol was expelled, water added, and then the mixture extracted with ether. After evaporation of the ether the residue was treated with steam as long as an oil passed over, the distillate shaken out with ether, and the ethereal solution dried and fractionated. The fraction under 200° contained benzoic aldehyde, but a larger portion passed over between 204°–208°, and consisted of benzoic ether.

The formation of benzoic aldehyde by the intercession of alcohol is easily explained, as will be seen from the following equations:

$$C_6H_5CHOHCOC_6H_5 + C_2H_5OH = C_6H_5CH\begin{matrix}OC_2H_5\\OH\end{matrix} + C_6H_5CHO$$

$$C_6H_5CH\begin{matrix}OC_2H_5\\OH\end{matrix} = C_6H_5CHO + C_2H_5OH.$$

In order to explain the formation of ethyl benzoate it is necessary to assume that it is due to the action of alcoholic hydrocyanic acid on the aldehyde. That benzoic ether is really formed by the action of alcoholic hydrocyanic acid on benzoic aldehyde is proven by the experiment described below. It is certainly an interesting fact that starting with benzoic aldehyde by the use of potassium cyanide it can be converted into its carbon-polymer, while the proper use of the free acid will re-convert the latter compound, at least partially, into the original aldehyde.

Action of Hydrocyanic Acid on Benzoic Aldehyde.

The formation of the nitrile of mandelic acid by the action of hydrocyanic acid on the aldehyde at a moderate temperature indicated that in order that the peculiar reducing and oxidising property of the acid should show itself, it would be necessary to allow the action to take place at a high temperature. We have found that the products of the reaction differ according to whether alcohol or water is used.

Two grams benzoic aldehyde, some absolute alcohol, and a small quantity of hydrocyanic acid were heated in a sealed tube to 190°–200° for five hours. After evaporating the alcohol, the residual oil was shaken with acid sulphite of sodium and then extracted with ether. The oil, which remained after the ether was expelled, was tested with acid sulphite for unchanged aldehyde, and found to be free of it. It consisted of ethyl benzoate, as was shown by decomposing with caustic potash, and proving the formation of benzoic acid. About three-quarters of a gram of acid was obtained. It seems probably that benzyl alcohol was also formed in this reaction, as is the case when alcoholic potash acts on the aldehyde.[1] The experiment will be repeated on a larger scale, with a view of isolating the other products of the reaction, if such are formed. In the experiment using alcohol instead of water, four grams of the aldehyde, water and one cc. hydrocyanic acid were heated for five hours at 190°–200°. The insoluble oil was shaken with $NaHSO_3$, then the mixture with ether, which dissolved in oil, having the smell of stryol.

The action of water on benzoic aldehyde at a high temperature was also examined. Two grams aldehyde and water were heated in a sealed tube to 200° for five hours. On treating the contents of the tube as already described, a small amount of benzoic acid was obtained. The quantity, however, was so small that its formation may have been due to the air contained in the tube.

We have also made several experiments on the action of nascent hydrocyanic acid on warm alcoholic solution of phenanthrenequinone, and have obtained a product quite different from that obtained by Japp and Miller.[2] The product is, if the reaction has proceeded like the analogous diketone already studied, the ether of the half aldehyde of dephenic acid. We shall return to the subject in another paper.

We believe that these experiments suffice to show that hydrocyanic acid possesses in a most marked degree the property of causing certain organic substances susceptible of oxidation and reduction to assimilate the elements of water or alcohol, thereby undergoing a simultaneous oxidation and reduction; and even make it probable that all such compounds will, under the proper conditions of experiment, undergo a corresponding change. We shall continue our investigation in the line already indicated.

TUFTS COLLEGE, *Sept.* 20*th*, 1885.

[1] Cannizzaro, Annalen **88**, 129.

[2] Berichte, 1883, 2418.

ON THE ACTION OF ALKYL IODIDES ON AMIDO ACIDS.

By Arthur Michael and John F. Wing.

Although it has been known for some years that the intensity with which alkyl iodides enter into reactions differs, to a certain degree, according to the iodide used, it is only lately that this subject has been systematically investigated. Wislicenus[1] has shown that in their action on sodium acet-acetate the iodides of primary radicles show the greatest, the tertiary the least activity; while in the homologous series the iodides of a lower series seem to have relatively a greater activity than that of a higher. It would seem as if this property would show itself, not only quantitatively but also qualitatively, in some of the reactions of the iodides; as yet, however, hardly any facts are known that tend to indicate it. While engaged in the investigation of the action of methyl iodide on asparagine[2] we made a corresponding experiment with ethyl iodide, and were surprised to find a marked difference in the two reactions. This suggested to us that the amido acids are a class of compounds with properties particularly adapted to the examination of the activity of the alkyl iodides; for, evidently, if the iodides shall show qualitative differences in their action on the same substance, this is most likely to occur when bodies are employed that have but a slight affinity for them. P. Griess[3] has noticed, in fact, a qualitative difference in one instance; for he found that when ethyl iodide is heated with potassium metamidobenzoate the mono and diethyl derivatives are formed, no matter in what proportion the reagents are used, while allyl iodide gave only the disubstitution product when the reagents were taken in molecular proportion.

Action of Methyl Iodide on Potassium Paramidobenzoate.

According to Griess,[4] an excess of methyl iodide acts on potassium metamidobenzoate forming the betaine, a strong base that decomposes on distilling into the isomeric dimethylamidobenzoic methyl ether.

[1] Annalen **212**, 239. [2] This Journal **6**, 419. [3] Berichte, 1872, 1038. [4] *Ibid.* 1873, 585.

For the purpose of examining its action on the para acid, an excess of caustic potash was added to a solution of the acid in methyl alcohol, and then three times the molecular proportion of methyl iodide. This mixture was allowed to stand for four days, during which time further quantities of alkali were added as the solution became neutral. The liquid was then poured off from the potassium iodide that had separated, and evaporated to dryness on the water-bath. After dissolving in water an excess of acetic acid was added, which precipitated the mono and disubstitution products. The filtrate from this acid was evaporated until the greater part of potassium iodide was precipitated, and the filtrate treated with an excess of hydriodic acid. This gave a precipitate consisting of the iodhydrate and periodide of the betaine. These two substances were separated by crystallising from water, the periodide being insoluble it crystallised out on cooling. It consists of long dark prisms, and melts at 200°. On evaporating the filtrate sufficiently and cooling, the iodhydrate was deposited. It has about the same solubility as potassium iodide.

An iodine estimation of the salt gave the following figures:

0.3045 gram of substance gave 0.2333 gram of AgI.

	Theory for $C_6H_4\begin{cases}N(CH_3)_3HI.\\CO>O\end{cases}$	Found.
I	41.37	41.40

The salt consists of short, yellowish, rectangular plates, melting at 233°. The addition of platinum chloride to a dilute hydrochloric acid solution of it gave the double platinum salt, which forms large red prisms. A platinum estimation gave as follows:

0.356 gram of substance gave 0.0915 gram of Pt.

	Theory for $\left(C_6H_4\begin{matrix}N(CH_3)_3H\\CO>O\end{matrix}\right)_2PCl_4$.	Found.
Pt	25.6	25.7

To obtain the free betaine an aqueous solution of the salt was treated with an excess of freshly precipitated silver oxide, filtered, and the filtrate evaporated to dryness. The base was then extracted by hot alcohol, from which it was deposited on cooling. It contains water of crystallisation. On analysing, the following results were obtained:

0.2885 gram of substance, air-dried, lost 0.0265 gram of H_2O at 100°.

0.2672 gram of substance, dried at 100°, gave 0.6589 gram of CO_2 and 0.1725 gram of H_2O.

	Theory for $C_6H_4<\overset{N(CH_3)_3}{\underset{CO}{>O}}$.	Found.
C	67.04	67.24
H	7.26	7.17

	Theory for $C_6H_4<\overset{N(CH_3)_3}{\underset{CO}{>O}}H_2O$.	Found.
H_2O	9.14	9.18

The betaine crystallises from alcohol as colorless plates that melt at about 255°. It is readily soluble in water, and forms salts with organic acids, as acetic acid.

The precipitate obtained by addition of acetic acid was found to consist of almost pure dimethylamidobenzoic acid, and melted, without further crystallisation, at 234°. This substance has been already examined by W. Michler,[1] who obtained the mono and diproducts in the action of methyl iodide on amidobenzoate, using the proportion of one molecule of the first to two of the latter compound. An analysis was made:

0.300 gram of acid gave 0.1935 gram of H_2O and 0.7228 gram of CO_2.

	Theory for $C_6H_4\overset{N(CH_3)_2}{COOH}$.	Found.
C	65.40	65.70
H	6.60	7.1

Action of Ethyl Iodide on Potassium Paramidobenzoate.

Two separate portions of the reaction, obtained in somewhat different manner, were accidentally mixed, and worked up together. In one portion ten grams of paramidobenzoic acid dissolved in alcohol was treated with an excess of caustic potash, three times the molecular weight of ethyl iodide, and allowed to stand for four days; in the second a larger proportion of ethyl iodide and alkali were allowed to act for two weeks on four grams of acids. In each case a further quantity of alkali was added as soon as the solutions became neutral. The mixture was heated until free of alcohol and water added to the residue. It was found not to be completely soluble; a heavy oil remaining undissolved. The liquid was extracted with ether, which dissolved the oil, and the extract, after drying over $CaCl_2$, fractionated. Between 312°-

[1] Berichte, 1876, 402.

315° the oil passed over without decomposition. An analysis was as follows:

0.3081 gram of oil gave 0.2502 gram of H_2O and 0.7969 gram of CO_2.

	Theory for $C_6H_4{}^{N(C_2H_5)_2}_{COOC_2H_5}$.	Found.
C	70.59	70.50
H	8.59	9.02

The ether solidifies in a freezing mixture of salt and ice, and is readily soluble in alcohol and ether, insoluble in water. It dissolves in acids to form the corresponding salts, all of which, including the iodhydrate, are soluble in water. Boiled with alcoholic potash, the alcohol driven off and acetic acid added, it gave a precipitate of diethylamidobenzoic acid. The formation is represented by the equation:

$$C_6H_4{}^{NH_2}_{COOK} + 3C_2H_5I + 2KOH = C_6H_4{}^{N(C_2H_5)_2}_{COOC_2H_5} + 3KI + 2H_2O.$$

The liquid remaining after extracting with ether was acidulated with acetic acid, and gave a precipitate which consisted solely of diethylamidobenzoic acid. It agreed in its properties with those given by Michler and Gradmann,[1] who obtained it by heating the amidobenzoate with ethyl iodide. For further identification a portion was analysed:

0.1943 gram of substance gave 0.4842 gram of CO_2 and 0.1335 of H_2O.

	Theory for $C_6H_4{}^{N(C_2H_5)_2}_{COOH}$.	Found.
C	68.39	67.95
H	7.77	7.83

If the betaine were formed it should have been contained in the filtrate from the diethyl derivative, but the liquid was carefully examined for it without success. It might be thought that the oil contained some, but before distilling it dissolved completely in hydriodic acid, thereby showing its absence.

Action of Allyl Iodide on Potassium Paramidobenzoate.

In this experiment a quantity of acid was dissolved in alcohol, an excess of alkali added, and then three times the molecular

[1] Berichte, 1876, 1912.

proportion of allyl iodide. Like in the preceding experiments, the solution was kept alkaline, and allowed to stand for four days. The residue remaining after evaporation of alcohol dissolved completely in water, and the solution was acidulated with acetic acid. For analysis the precipitate was crystallised several times from alcohol:

0.2546 gram of substance gave 0.671 gram of CO_2 and 0.1509 gram of H_2O.

	Theory for $C_6H_4{}^{N(C_3H_5)_2}_{COOH}$.	Found.
C	71.89	71.87
H	6.91	6.58

Diallylparamidobenzoic acid crystallises in short, yellowish prisms, melting at 127°. It is insoluble in water, quite readily in hot alcohol. Alkalis and acid dissolve it to form the corresponding salts. This acid is the sole product of the action of allyl iodide on paramidobenzoate. We were unable to find any indication that either the betaine or that the allyl ether of the acid were formed.

By comparing these results it will be seen that each of the alkyl iodides examined in regard to its behavior to paramidobenzoic acid acts in a manner peculiar to itself. While methyl iodide, under the above-described conditions, yielded dimethylamidobenzoic acid and the betaine, the ethyl compound was found to form instead of the betaine its isomer, diethylamidobenzoic ether. A reason for this different behavior may be that the ethyl betaine cannot exist, perhaps undergoes already at ordinary temperature the same decomposition that the methyl betaine does at its boiling point. Finally, it was found that allyl iodide, under the same conditions, yielded neither a betaine nor the corresponding ether, and in this case the sole product is the diallyl derivative.

These results are of interest as showing that the alkyl iodides do not necessarily show the same reactions. We shall endeavor to ascertain whether they are capable of generalisation with other amido acids, and will also examine the action of alkyl iodides of higher series.

TUFTS COLLEGE, MASS., *Sept. 30th*, 1885.

REVIEWS AND REPORTS.

Recent Researches on the Pyridine and Quinoline Bases.

Pyridine Series, $C_nH_{2n-5}N$.—Since the appearance of the last report on these bases in this Journal,[1] additional methods of obtaining pyridine and its derivatives have been discovered. Lieben and Haitinger[2] have treated chelidonic acid with ammonia and distilled the resulting compound with zinc dust. Pyridine was found among the distillation products. Meconic acid was treated in the same way and it also yielded pyridine. By simple transformations, Ost[3] converted meconic acid into picolinic acid. Haitinger[4] has also found that dehydracetic acid can be made to undergo changes similar to those by means of which chelidonic and meconic acids are converted into pyridine. If treated with ammonia, dehydracetic acid is converted into a nitrogenous basic compound, which when distilled with zinc dust yields lutidine.

These reactions are of great interest because they are instances of the simple transformation of non-nitrogenous organic compounds into pyridine derivatives. It is highly probable that the alkaloids and albuminous substances are built up in plants from similar compounds and in a similar way. When we consider that chelidonic and meconic acids occur in plant juices, and that ammonia and nitrates are also present, we can readily understand how reactions of this kind must be of great value in giving an insight into the chemical processes which accompany the assimilation of nitrogen in plant organisms. One of the most characteristic reactions of this kind has been discovered by von Pechmann,[5] who obtained oxynicotinic acid by the action of ammonia upon cumalinic acid. Cumalinic acid is a condensation product obtained by the action of sulphuric acid upon malic acid. When treated with ammonia, water is eliminated, and oxynicotinic acid formed according to the equation:

$$C_5H_3O_2COOH + NH_3 = H_2O + C_5H_3N\langle^{COOH}_{OH}$$

Cumalinic acid. Oxynicotinic acid.

Chelidonic acid acts in an analogous manner, giving oxypyridine-dicarbonic acid.

$$C_5H_3O_2COOH + NH_3 = H_2O + C_5H_2N\langle^{(COOH)_2}_{OH}$$

Chelidonic acid. Oxypyridine-dicarbonic acid.

[1] Vol. **5**, 60. [2] Berichte der deutschen chem. Gesell. **16**, 1959, 1963.
[3] Journal für praktische Chemie, 1883, **136**, 257.
[4] Berichte der deutschen chem. Gesell. **18**, 452. [5] *Ibid.* **17**, 2384.

Closely related to these investigations is the work of Behrmann and Hofmann[1] upon the amides of citric acid. These investigators observed that when citramide is treated with sulphuric acid, under certain conditions, it is converted into dioxypyridine-carbonic acid. The latter substance was, by means of phosphorus pentachloride, transformed into dichlorpyridine-carbonic acid, which, on being reduced with hydriodic acid, gave isonicotinic acid.

Beside these reactions of general interest, pyridine derivatives have been obtained by a number of other methods. Waage[2] has obtained a parvoline by the action of heat upon propionic aldehyde ammonia. Hofmann[3] obtained collidine by heating glycol and ammonium chloride to a temperature of 190° in sealed tubes. Ethylidene chloride and ethyl amine treated in the same way also gave collidine. Hofmann has also described a general reaction for the detection of minute quantities of pyridine and its homologues. A few drops of the base to be examined are heated with an equal volume of methyl iodide in a test tube, and pulverised caustic soda or potash added to form a thick paste. If the mixture be gently heated, and pyridine bases are present, a vapor of a highly characteristic but not unpleasant odor will be produced. Ost[4] has found that commercial ammonia frequently contains pyridine, and from one sample of crude ammonia weighing 2½ kilos he obtained several grams of pyridine platinum chloride.

Ladenburg[5] has developed a general method for the synthesis of the homologous pyridine bases. The method is based upon a reaction which Hofmann first used in preparing the homologues of aniline. It consists in making the alkyl addition products of pyridine, and subjecting the resulting compounds to a high temperature in sealed tubes. The addition product is thus changed into the hydriodic acid salt of a substituted pyridine. Ethyl pyridinium iodide was heated in a sealed tube to the temperature of melting lead, and there were formed two isomeric ethyl-pyridines. In the same way two propyl pyridines[6] or collidines were obtained from propylpyridinium iodide.

Piperidine Series, $C_nH_{2n+1}N$.—In the last report[7] it was mentioned that piperidine was regarded as a hexahydropyridine. Our knowledge concerning this subject has been largely extended by the labors of Hofmann and Ladenburg. The intimate relationship existing between these bases has been thoroughly established, and ready means of converting the one into the other have been described. In 1877 Hofmann[8] treated piperidine with bromine and obtained a dibrom-pyridine. This fact led him to suspect that a close connection existed between the two bases. Subsequently Königs[9] confirmed this idea by obtaining pyridine as an oxidation product of piperidine. The transformation was, however,

[1] Berichte der deutschen chem. Gesell. **17**, 2681. [2] Monatshefte für Chemie **4**, 708.
[3] Berichte der deutschen chem. Gesell. **17**, 1905, 1907, 1909.
[4] Journal für praktische Chemie **136**, 271.
[5] Berichte der deutschen chem. Gesell. **16**, 1410, 2059. [6] *Ibid.* **17**, 772.
[7] This Journal **5**, 63. [8] Berichte der deutschen chem. Gesell. **10**, 984. [9] *Ibid.* **12**, 2341.

exceedingly difficult. Ordinary oxidising agents gave no results, and it was only by treating the piperidine with concentrated sulphuric acid at a temperature of 300° that a very small quantity of pyridine, hardly sufficient for analysis, was obtained. Hofmann,[1] in again taking up the subject, expressed the opinion that the action of bromine upon piperidine consisted, primarily, in the removal of hydrogen, giving pyridine; and then, as a secondary action, the bromine acted upon the pyridine and gave dibrompyridine. He endeavored, therefore, by working under different conditions to stop the reaction at the end of the first stage. For this purpose piperidine acetate was treated with bromine in the proportion of one molecule of the former to two of the latter. Pyridine was found among the reaction products in considerable quantity.

The comparative ease with which piperidine was thus transformed into pyridine led Hofmann to attempt the reverse change of pyridine into piperidine. Königs,[2] previous to this time, claimed to have obtained some piperidine by reducing pyridine with tin and hydrochloric acid, but his work left much to be desired, and Hofmann therefore tried to obtain better results by using concentrated hydriodic acid. At temperatures above 300° the acid acted upon the pyridine, but no piperidine was formed; the reducing action was too energetic, and normal pentane and ammonia were the products. Ladenburg[3] was the next to take up the problem, and he began by carefully repeating the experiments of Königs. He subjected pyridine to the reducing action of tin and hydrochloric acid under various conditions, but in no case was piperidine formed. After making a great many experiments he found that by treating an alcoholic solution of pyridine with metallic sodium, piperidine was readily formed. The reaction was found to be almost quantitative, and large quantities of synthetical piperidine were prepared. Its properties were then thoroughly compared with those of the piperidine obtained from the piperine of pepper, and their identity was established beyond doubt.

Ladenburg[4] then applied this reduction process to the other pyridine bases. The picolines, lutidines, and collidines were converted into hexahydro-derivatives which are homologues of piperidine. In naming the members of this new homologous series he uses terms which indicate their derivation as well as their relation to the corresponding members of the pyridine series. Thus we have:

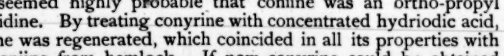
Pyridine C_5H_5N	Piperidine $C_5H_{10}NH$
Picoline $C_5H_4(CH_3)N$	Pipecoline $C_5H_9(CH_3)NH$
Lutidine $C_5H_3(CH_3)_2N$	Lupetidine $C_5H_8(CH_3)_2NH$
Collidine $C_8H_{11}N$	Copellidine $C_8H_{17}N$.

Within the last two years the alkaloid coniine has been made synthetically. In 1880 Wischnegradsky[5] obtained a pyridine

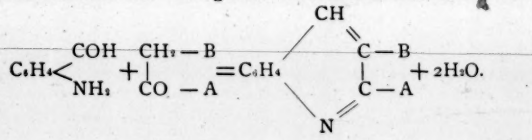
[1] Berichte der deutschen chem. Gesell. **16**, 588. [2] *Ibid.* **14**, 1856. [3] *Ibid.* **17**, 156.
[4] *Ibid.* **18**, 913, 920. [5] *Ibid.* **18**, 2316.

carbonic acid as one of its oxidation products. After the formula of coniine was found to be $C_8H_{17}N$, it was suspected that it might be a propyl derivative of piperidine. There was no experimental basis for this view, however, until last year, when Hofmann[1] distilled coniine hydrochloride with zinc dust and obtained a base $C_8H_{11}N$ which he called conyrine. Oxidised with potassium permanganate, conyrine was converted into picolinic acid. It therefore seemed highly probable that coniine was an ortho-propyl piperidine. By treating conyrine with concentrated hydriodic acid, coniine was regenerated, which coincided in all its properties with the coniine from hemlock. If now conyrine could be obtained by the introduction of a propyl group into pyridine the synthesis of coniine would be complete. This has been accomplished by Ladenburg,[2] who, by means of his general reaction for making the homologous pyridine bases, succeeded in making an isopropyl pyridine which is identical with conyrine. On reducing this compound with metallic sodium in an alcoholic solution, a hexahydroisopropyl piperidine was obtained, which, in all its properties, physiological as well as physical, is perfectly identical with coniine. As would be expected the synthetical coniine is not optically active.

Quinoline Series, $C_nH_{2n-11}N$.—A general method for the synthesis of quinoline derivatives has been discovered by Friedländer.[3] It consists in bringing together orthoamidobenzoic aldehyde with any aldehyde or ketone in the presence of dilute caustic soda. If acetic aldehyde is used, quinoline is obtained according to the equation:



Further study[4] of the reaction showed that it was not limited to acetic aldehyde, but that a whole series of aldehydes and ketones could, by means of orthoamidobenzoic adehyde, be converted into quinoline derivatives. The general reaction is as follows:



When acetone was used an α-methyl-quinoline or quinaldine was obtained. Acetophenone gave an α-phenyl-quinoline, phenylacetic aldehyde gave β-phenyl-quinoline, etc.

[1] Berichte der deutschen chem. Gesell. **17**, 823. [2] *Ibid.* **17**, 1123, 1676. [3] *Ibid.* **15**, 2573. [4] *Ibid.* **16**, 1833.

The synthetical reaction of Doebner and von Miller[1] has also been found to be capable of extensive application in the preparation of substituted quinolines. When ethylene alcohol or paraldehyde is heated with aniline and concentrated hydrochloric acid, a methyl-quinoline or quinaldine is formed. The most probable explanation of the reaction is that crotonic aldehyde is first formed, which then acts upon the aniline and gives an *a*-methyl-quinoline. By starting with substituted anilines, such as the toluidines, xylidines, etc., substituted quinaldines having the substituting groups in the benzene portion of the compound are obtained. On the other hand, if instead of acetic aldehyde, other aldehydes such as propionic, butyric or valeric aldehyde be taken, then the resulting compounds will be quinaldines having the substituting groups in the pyridine portion of the compound. A large number of such derivatives have been obtained and studied.

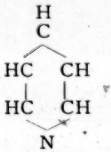
The question of the identity or isomerism of the quinoline obtained from cinchonine, and the leucoline from coal-tar or bone-oil, may now be regarded as definitely settled. The only reason for regarding them as isomeric compounds was that the cinchonine-quinoline, when treated with amyl iodide and caustic alkalis, gave the blue coloring matter known as cyanine. In 1879 Hoogewerff and van Dorp,[2] however, obtained the same pyridine dicarbonic acid by oxidising quinoline and leucoline. From their experiments it seemed highly probable that the formation of cyanine was due to the presence of some foreign substance in the quinoline. They[3] have subsequently verified this suspicion by subjecting cinchonine-quinoline to repeated fractional distillation, and then converting it into the chromic acid salt. After a great many recrystallisations the salt was decomposed with caustic soda, and the pure quinoline thus obtained when treated with amyl iodide gave no indication of the formation of cyanine. Cyanine is only produced by the action of amyl iodide upon a mixture of quinoline and lepidine. Quinoline, therefore, from whatsoever source it is obtained, whether from the alkaloids, from bone-oil or coal-tar, or by means of synthetical reactions, is one and the same substance.

Very recently, however, Hoogewerff and van Dorp[4] have found that quinoline in crude bone-oil is accompanied by an isomeric substance. The crude bone-oil quinoline was dissolved in twice its weight of alcohol (95-96 per cent.), and a quantity of concentrated sulphuric acid necessary to convert the base into the acid sulphate salt was added. The solution was allowed to cool, and the acid sulphate salt which separated was decomposed by caustic potash. The basic oil thus obtained was separated by repeated fractional

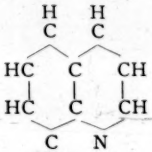
[1] Berichte der deutschen chem. Gesell. **17**, 1698, 1712.
[2] *Ibid.* **16**, 425.
[3] Recueil des Travaux Chimiques **1**, 1, **2**, 28, 41.
[4] *Ibid.* **4**, 125.

distillation into two parts. One of these boiled from 230° to 236°, and consisted for the most part of quinoline. The other part boiled from 236° to 243°, and contained the new base. This fraction was converted into the sulphate, and recrystallised from alcohol until it fused at a temperature of 200°. The base obtained from the crystalline salt boiled at 236° to 237½° (not corrected); at ordinary temperatures it solidifies in the form of plates which melt at 18° to 23°. Analyses of the compound itself, as well as those of its salts, correspond with the composition expressed by the formula C_9H_7N. It is therefore an isoquinoline.

A consideration of the properties of pyridine and quinoline led Körner in 1870 to suggest that these bases might be analogous to benzene and naphthalene in constitution, that is, their formulae might be represented by closed chains, thus:



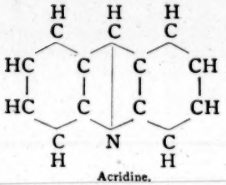
Pyridine.



Quinoline.

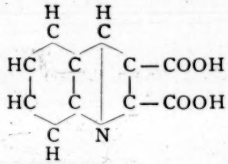
Körner, however, never published this idea. It has been attributed to him by various German writers. Baeyer in his paper on synthetical picolines in Liebig's Annalen for June, 1870, was the first to call attention to it. In the following year Dewar[1] published the same idea. These formulae have been generally accepted. The intimate connection existing between the two bases, their methods of synthesis and transformation into one another, as well as their relation to the benzene hydrocarbons, all seem to be best explained by the assumption of these ring formulæ. The question has recently been raised whether the nitrogen in these compounds is united with three or with two carbon atoms. Riedel[2] has brought forward reasons for believing the former view to be more probable. They are as follows: Graebe and Caro[3] discovered a new base which they called acridine, accompanying crude anthracene. By oxidation acridine was converted into acridinic acid, which by further decomposition was changed into β-quinoline-carbonic acid. Riedel, who had determined the constitution of β-quinoline-carbonic acid, called attention to the fact that the formation of this acid from acridine could only be accounted for by assuming that the latter compound had this formula:

[1] Chemical News, 1871, **23**, 40. [2] Berichte der deutschen chem. Gesell. **16**, 1609.
[3] Liebig's Annalen der Chemie **158**, 265.



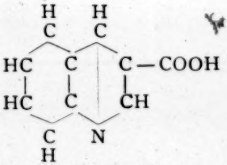
Acridine.

By oxidation we would then obtain acridinic acid :



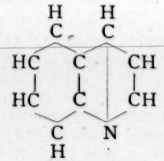
Acridinic acid.

which by heat would be converted into β-quinoline carbonic acid :

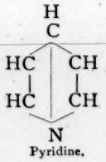


β-quinoline-carbonic acid.

Pyridine and quinoline would then be represented by the following formulae :



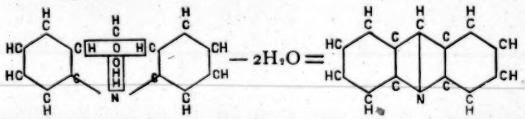
Quinoline.



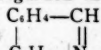
Pyridine.

This view has obtained further support in the recent synthesis of acridine from diphenylamine and formic acid by Bernthsen and

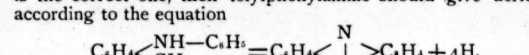
Bender.[1] When diphenylamine and formic acid are brought together in the presence of zinc chloride, a base of the formula $C_{13}H_9N$ having all the properties of acridine is formed. The authors represent the action as follows:



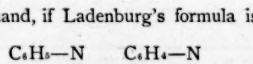
Ladenburg[2] has suggested that acridine may be regarded as related to carbazol, and represents the formula thus



Pyridine would then retain the formula suggested by Körner. To decide between these formulae, Graebe passed tolylphenylamine and benzylideneamine through heated tubes. If Riedel's formula is the correct one, then tolylphenylamine should give acridine according to the equation



On the other hand, if Ladenburg's formula is correct we would have

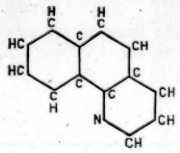


Benzylideneamine.

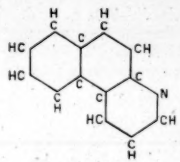
The experiment showed that the first reaction took place with an abundant yield of acridine, while none could be obtained from the benzylideneamine. All facts known at present are therefore in accordance with the former view of the constitution of acridine.

The question of the relative position of substituting groups with reference to the nitrogen atom in mono-substitution products of pyridine is still an open one. It is highly desirable that the three pyridine-monocarbonic acids, which are so well known, should be classified as ortho, meta and para derivatives. Considerable work has been done in this direction, but not sufficient to warrant drawing definite conclusions. In brief, the problem stands to-day as follows: Skraup,[3] by applying his method for the synthesis of quinoline to α- and β-naphthylamine, obtained α- and β-naphthoquinoline. These compounds, from their method of formation, we are justified in assuming, have the following formulae:

[1] Berichte der deutschen chem. Gesell. **16**, 1803. [2] *Ibid.* **16**, 2061.
[3] Monatshefte für Chemie **4**, 436.

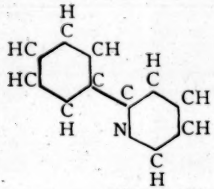


α-naphthoquinoline.

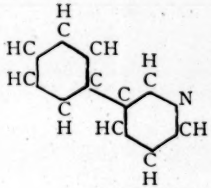


β-naphthoquinoline.

By oxidation of these compounds, acids were formed which on being decomposed gave α- and β-phenylpyridine respectively.



α-phenyl-pyridine.



β-phenyl-pyridine.

Further oxidation of these substances converted the former into picolinic acid and the latter into nicotinic acid. Picolinic acid would therefore be an ortho compound, nicotinic acid a meta compound, while the remaining acid, or isonicotinic acid would necessarily be a para derivative. Hoogewerff and van Dorp[1] have, however, raised an objection to this classification, because it was found that there are three pyridine dicarbonic acids which can be converted into isonicotinic acid. If isonicotinic acid is a para compound there can be, theoretically, but two pyridine dicarbonic acids which could be converted into it. The three acids which can be converted into isonicotinic acid are cinchomeronic, lutidinic and Böttinger's pyridine-dicarbonic acids. Skraup, in replying to Hoogewerff and van Dorp's objection to his classification, stated that it would probably be found that Böttinger's dicarbonic acid is identical with cinchomeronic acid. Voigt[2] recently prepared Böttinger's acids for the purpose of making this comparison, and found that these two acids are isomeric compounds of totally different properties, and that there are three pyridine-dicarbonic acids which can be converted into isonicotinic acid. So that the constitution of these three acids is still undetermined, although they are the best known and most thoroughly studied of all pyridine derivatives.

E. H. KEISER.

[1] Berichte der deutschen chem. Gesell. **14**, 646.
[2] Annalen der Chemie **228**, 51.